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# Chemical Engineering Design

R. K. SINNOTT



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## CHAPTER 1

# *Introduction to Design*

### 1.1. INTRODUCTION

This chapter is an introduction to the nature and methodology of the design process, and its application to the design of chemical manufacturing processes.

### 1.2. NATURE OF DESIGN

This section is a general, somewhat philosophical, discussion of the design process; how a designer works. The subject of this book is chemical engineering design, but the methodology of design described in this section applies equally to other branches of engineering design.

Design is a creative activity, and as such can be one of the most rewarding and satisfying activities undertaken by an engineer. It is the synthesis, the putting together, of ideas to achieve a desired purpose. The design does not exist at the commencement of the project. The designer starts with a specific objective in mind, a need, and by developing and evaluating possible designs, arrives at what he considers the best way of achieving that objective; be it a better chair, a new bridge, or for the chemical engineer, a new chemical product or a stage in the design of a production process.

When considering possible ways of achieving the objective the designer will be constrained by many factors, which will narrow down the number of possible designs; but, there will rarely be just one possible solution to the problem, just one design. Several alternative ways of meeting the objective will normally be possible, even several best designs, depending on the nature of the constraints.

These constraints on the possible solutions to a problem in design arise in many ways. Some constraints will be fixed, invariable, such as those that arise from physical laws, government regulations, and standards. Others will be less rigid, and will be capable of relaxation by the designer as part of his general strategy in seeking the best design. The constraints that are outside the designer's influence can be termed the external constraints. These set the outer boundary of possible designs; as shown in Figure 1.1. Within this boundary there will be a number of plausible designs bounded by the other constraints, the internal constraints, over which the designer has some control; such as, choice of process, choice of process conditions, materials, equipment.

Economic considerations are obviously a major constraint on any engineering design: plants must make a profit.

Time will also be a constraint. The time available for completion of a design will usually limit the number of alternative designs that can be considered.

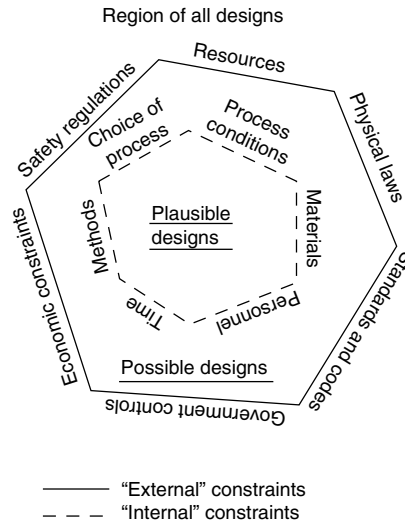


Figure 1.1. Design constraints

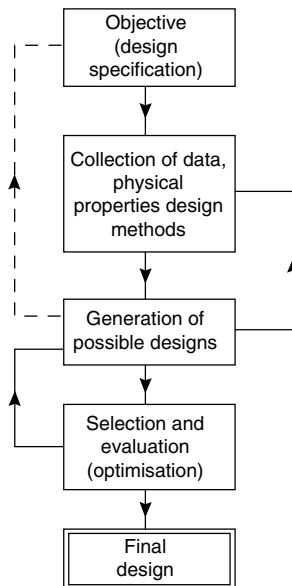


Figure 1.2. The design process

The stages in the development of a design, from the initial identification of the objective to the final design, are shown diagrammatically in Figure 1.2. Each stage is discussed in the following sections.

Figure 1.2 shows design as an iterative procedure; as the design develops the designer will be aware of more possibilities and more constraints, and will be constantly seeking new data and ideas, and evaluating possible design solutions.

### **1.2.1. The design objective (the need)**

Chaddock (1975) defined design as, the conversion of an ill-defined requirement into a satisfied customer.

The designer is creating a design for an article, or a manufacturing process, to fulfil a particular need. In the design of a chemical process, the need is the public need for the product, the commercial opportunity, as foreseen by the sales and marketing organisation. Within this overall objective the designer will recognise sub-objectives; the requirements of the various units that make up the overall process.

Before starting work the designer should obtain as complete, and as unambiguous, a statement of the requirements as possible. If the requirement (need) arises from outside the design group, from a client or from another department, then he will have to elucidate the real requirements through discussion. It is important to distinguish between the real needs and the wants. The wants are those parts of the initial specification that may be thought desirable, but which can be relaxed if required as the design develops. For example, a particular product specification may be considered desirable by the sales department, but may be difficult and costly to obtain, and some relaxation of the specification may be possible, producing a saleable but cheaper product. Whenever he is in a position to do so, the designer should always question the design requirements (the project and equipment specifications) and keep them under review as the design progresses.

Where he writes specifications for others, such as for the mechanical design or purchase of a piece of equipment, he should be aware of the restrictions (constraints) he is placing on other designers. A tight, well-thought-out, comprehensive, specification of the requirements defines the external constraints within which the other designers must work.

### **1.2.2. Data collection**

To proceed with a design, the designer must first assemble all the relevant facts and data required. For process design this will include information on possible processes, equipment performance, and physical property data. This stage can be one of the most time consuming, and frustrating, aspects of design. Sources of process information and physical properties are reviewed in Chapter 8.

Many design organisations will prepare a basic data manual, containing all the process “know-how” on which the design is to be based. Most organisations will have design manuals covering preferred methods and data for the more frequently used, routine, design procedures.

The national standards are also sources of design methods and data; they are also design constraints.

The constraints, particularly the external constraints, should be identified early in the design process.

### **1.2.3. Generation of possible design solutions**

The creative part of the design process is the generation of possible solutions to the problem (ways of meeting the objective) for analysis, evaluation and selection. In this activity the designer will largely rely on previous experience, his own and that of others.

It is doubtful if any design is entirely novel. The antecedence of most designs can usually be easily traced. The first motor cars were clearly horse-drawn carriages without the horse; and the development of the design of the modern car can be traced step by step from these early prototypes. In the chemical industry, modern distillation processes have developed from the ancient stills used for rectification of spirits; and the packed columns used for gas absorption have developed from primitive, brushwood-packed towers. So, it is not often that a process designer is faced with the task of producing a design for a completely novel process or piece of equipment.

The experienced engineer will wisely prefer the tried and tested methods, rather than possibly more exciting but untried novel designs. The work required to develop new processes, and the cost, is usually underestimated. Progress is made more surely in small steps. However, whenever innovation is wanted, previous experience, through prejudice, can inhibit the generation and acceptance of new ideas; the “not invented here” syndrome.

The amount of work, and the way it is tackled, will depend on the degree of novelty in a design project.

Chemical engineering projects can be divided into three types, depending on the novelty involved:

1. Modifications, and additions, to existing plant; usually carried out by the plant design group.
2. New production capacity to meet growing sales demand, and the sale of established processes by contractors. Repetition of existing designs, with only minor design changes.
3. New processes, developed from laboratory research, through pilot plant, to a commercial process. Even here, most of the unit operations and process equipment will use established designs.

The first step in devising a new process design will be to sketch out a rough block diagram showing the main stages in the process; and to list the primary function (objective) and the major constraints for each stage. Experience should then indicate what types of unit operations and equipment should be considered.

Jones (1970) discusses the methodology of design, and reviews some of the special techniques, such as brainstorming sessions and synectics, that have been developed to help generate ideas for solving intractable problems. A good general reference on the art of problem solving is the classical work by Polya (1957); see also Chittenden (1987). Some techniques for problem solving in the Chemical Industry are covered in a short text by Casey and Frazer (1984).

The generation of ideas for possible solutions to a design problem cannot be separated from the selection stage of the design process; some ideas will be rejected as impractical as soon as they are conceived.

#### **1.2.4. Selection**

The designer starts with the set of all possible solutions bounded by the external constraints, and by a process of progressive evaluation and selection, narrows down the range of candidates to find the “best” design for the purpose.

The selection process can be considered to go through the following stages:

Possible designs (credible)—within the external constraints.

Plausible designs (feasible)—within the internal constraints.

Probable designs—likely candidates.

Best design (optimum)—judged the best solution to the problem.

The selection process will become more detailed and more refined as the design progresses from the area of possible to the area of probable solutions. In the early stages a coarse screening based on common sense, engineering judgement, and rough costings will usually suffice. For example, it would not take many minutes to narrow down the choice of raw materials for the manufacture of ammonia from the possible candidates of, say, wood, peat, coal, natural gas, and oil, to a choice of between gas and oil, but a more detailed study would be needed to choose between oil and gas. To select the best design from the probable designs, detailed design work and costing will usually be necessary. However, where the performance of candidate designs is likely to be close the cost of this further refinement, in time and money, may not be worthwhile, particularly as there will usually be some uncertainty in the accuracy of the estimates.

The mathematical techniques that have been developed to assist in the optimisation of designs, and plant performance, are discussed briefly in Section 1.10.

Rudd and Watson (1968) and Wells (1973) describe formal techniques for the preliminary screening of alternative designs.

### 1.3. THE ANATOMY OF A CHEMICAL MANUFACTURING PROCESS

The basic components of a typical chemical process are shown in Figure 1.3, in which each block represents a stage in the overall process for producing a product from the raw materials. Figure 1.3 represents a generalised process; not all the stages will be needed for any particular process, and the complexity of each stage will depend on the nature of the process. Chemical engineering design is concerned with the selection and arrangement of the stages, and the selection, specification and design of the equipment required to perform the stage functions.

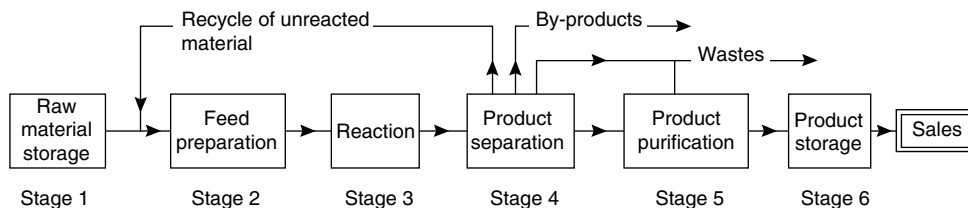


Figure 1.3. Anatomy of a chemical process

#### **Stage 1. Raw material storage**

Unless the raw materials (also called essential materials, or feed stocks) are supplied as intermediate products (intermediates) from a neighbouring plant, some provision will

have to be made to hold several days, or weeks, storage to smooth out fluctuations and interruptions in supply. Even when the materials come from an adjacent plant some provision is usually made to hold a few hours, or even days, supply to decouple the processes. The storage required will depend on the nature of the raw materials, the method of delivery, and what assurance can be placed on the continuity of supply. If materials are delivered by ship (tanker or bulk carrier) several weeks stocks may be necessary; whereas if they are received by road or rail, in smaller lots, less storage will be needed.

### ***Stage 2. Feed preparation***

Some purification, and preparation, of the raw materials will usually be necessary before they are sufficiently pure, or in the right form, to be fed to the reaction stage. For example, acetylene generated by the carbide process contains arsenical and sulphur compounds, and other impurities, which must be removed by scrubbing with concentrated sulphuric acid (or other processes) before it is sufficiently pure for reaction with hydrochloric acid to produce dichloroethane. Liquid feeds will need to be vaporised before being fed to gas-phase reactors, and solids may need crushing, grinding and screening.

### ***Stage 3. Reactor***

The reaction stage is the heart of a chemical manufacturing process. In the reactor the raw materials are brought together under conditions that promote the production of the desired product; invariably, by-products and unwanted compounds (impurities) will also be formed.

### ***Stage 4. Product separation***

In this first stage after the reactor the products and by-products are separated from any unreacted material. If in sufficient quantity, the unreacted material will be recycled to the reactor. They may be returned directly to the reactor, or to the feed purification and preparation stage. The by-products may also be separated from the products at this stage.

### ***Stage 5. Purification***

Before sale, the main product will usually need purification to meet the product specification. If produced in economic quantities, the by-products may also be purified for sale.

### ***Stage 6. Product storage***

Some inventory of finished product must be held to match production with sales. Provision for product packaging and transport will also be needed, depending on the nature of the product. Liquids will normally be dispatched in drums and in bulk tankers (road, rail and sea), solids in sacks, cartons or bales.

The stock held will depend on the nature of the product and the market.

### ***Ancillary processes***

In addition to the main process stages shown in Figure 1.3, provision will have to be made for the supply of the services (utilities) needed; such as, process water, cooling

water, compressed air, steam. Facilities will also be needed for maintenance, firefighting, offices and other accommodation, and laboratories; see Chapter 14.

### 1.3.1. Continuous and batch processes

Continuous processes are designed to operate 24 hours a day, 7 days a week, throughout the year. Some down time will be allowed for maintenance and, for some processes, catalyst regeneration. The plant attainment; that is, the percentage of the available hours in a year that the plant operates, will usually be 90 to 95%.

$$\text{Attainment \%} = \frac{\text{hours operated}}{8760} \times 100$$

Batch processes are designed to operate intermittently. Some, or all, the process units being frequently shut down and started up.

Continuous processes will usually be more economical for large scale production. Batch processes are used where some flexibility is wanted in production rate or product specification.

#### ***Choice of continuous versus batch production***

The choice between batch or continuous operation will not be clear cut, but the following rules can be used as a guide.

##### *Continuous*

1. Production rate greater than  $5 \times 10^6$  kg/h
2. Single product
3. No severe fouling
4. Good catalyst life
5. Proven processes design
6. Established market

##### *Batch*

1. Production rate less than  $5 \times 10^6$  kg/h
2. A range of products or product specifications
3. Severe fouling
4. Short catalyst life
5. New product
6. Uncertain design

## 1.4. THE ORGANISATION OF A CHEMICAL ENGINEERING PROJECT

The design work required in the engineering of a chemical manufacturing process can be divided into two broad phases.

*Phase 1.* Process design, which covers the steps from the initial selection of the process to be used, through to the issuing of the process flow-sheets; and includes the selection,



## CHEMICAL ENGINEERING

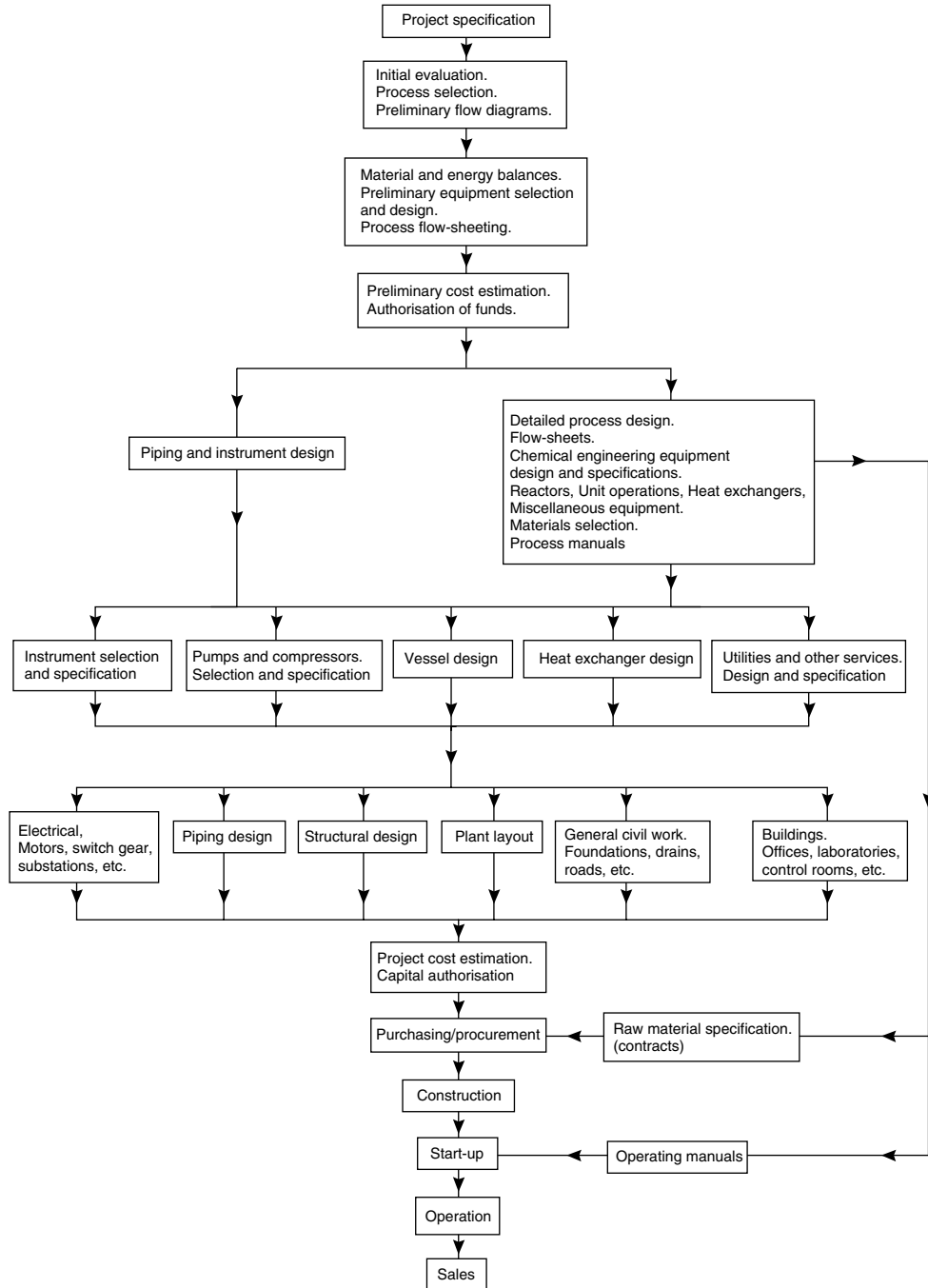


Figure 1.4. The structure of a chemical engineering project

specification and chemical engineering design of equipment. In a typical organisation, this phase is the responsibility of the Process Design Group, and the work will be mainly done by chemical engineers. The process design group may also be responsible for the preparation of the piping and instrumentation diagrams.

*Phase 2.* The detailed mechanical design of equipment; the structural, civil and electrical design; and the specification and design of the ancillary services. These activities will be the responsibility of specialist design groups, having expertise in the whole range of engineering disciplines.

Other specialist groups will be responsible for cost estimation, and the purchase and procurement of equipment and materials.

The sequence of steps in the design, construction and start-up of a typical chemical process plant is shown diagrammatically in Figure 1.4 and the organisation of a typical project group in Figure 1.5. Each step in the design process will not be as neatly separated from the others as is indicated in Figure 1.4; nor will the sequence of events be as clearly defined. There will be a constant interchange of information between the various design sections as the design develops, but it is clear that some steps in a design must be largely completed before others can be started.

A project manager, often a chemical engineer by training, is usually responsible for the co-ordination of the project, as shown in Figure 1.5.

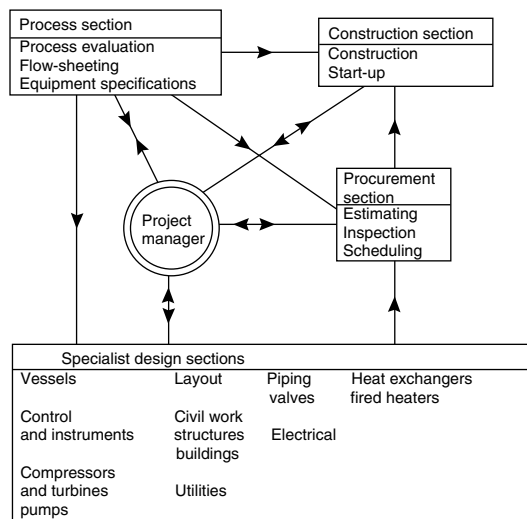


Figure 1.5. Project organisation

As was stated in Section 1.2.1, the project design should start with a clear specification defining the product, capacity, raw materials, process and site location. If the project is based on an established process and product, a full specification can be drawn up at the start of the project. For a new product, the specification will be developed from an economic evaluation of possible processes, based on laboratory research, pilot plant tests and product market research.

The organisation of chemical process design is discussed in more detail by Rase and Barrow (1964) and Baasel (1974).

Some of the larger chemical manufacturing companies have their own project design organisations and carry out the whole project design and engineering, and possibly construction, within their own organisation. More usually the design and construction, and possibly assistance with start-up, is entrusted to one of the international contracting firms.

The operating company will often provide the “know-how” for the process, and will work closely with the contractor throughout all stages of the project.

## 1.5. PROJECT DOCUMENTATION

As shown in Figure 1.5 and described in Section 1.4, the design and engineering of a chemical process requires the co-operation of many specialist groups. Effective co-operation depends on effective communications, and all design organisations have formal procedures for handling project information and documentation. The project documentation will include:

1. General correspondence within the design group and with:
  - government departments
  - equipment vendors
  - site personnel
  - the client
2. Calculation sheets
  - design calculations
  - costing
  - computer print-out
3. Drawings
  - flow-sheets
  - pipng and instrumentation diagrams
  - layout diagrams
  - plot/site plans
  - equipment details
  - pipng diagrams
  - architectural drawings
  - design sketches
4. Specification sheets
  - for equipment, such as:
    - heat exchangers
    - pumps
5. Purchase orders
  - quotations
  - invoices

All documents should be assigned a code number for easy cross referencing, filing and retrieval.

### ***Calculation sheets***

The design engineer should develop the habit of setting out calculations so that they can be easily understood and checked by others. It is good practice to include on calculation

sheets the basis of the calculations, and any assumptions and approximations made, in sufficient detail for the methods, as well as the arithmetic, to be checked. Design calculations are normally set out on standard sheets. The heading at the top of each sheet should include: the project title and identification number and, most importantly, the signature (or initials) of the person who checked the calculation.

### ***Drawings***

All project drawings are normally drawn on specially printed sheets, with the company name; project title and number; drawing title and identification number; draughtsman's name and person checking the drawing; clearly set out in a box in the bottom right-hand corner. Provision should also be made for noting on the drawing all modifications to the initial issue.

Drawings should conform to accepted drawing conventions, preferably those laid down by the national standards. The symbols used for flow-sheets and piping and instrument diagrams are discussed in Chapter 4. Drawings and sketches are normally made on detail paper (semi-transparent) in pencil, so modifications can be easily made, and prints taken.

In most design offices Computer Aided Design (CAD) methods are now used to produce the drawings required for all the aspects of a project: flow-sheets, piping and instrumentation, mechanical and civil work.

### ***Specification sheets***

Standard specification sheets are normally used to transmit the information required for the detailed design, or purchase, of equipment items; such as, heat exchangers, pumps, columns.

As well as ensuring that the information is clearly and unambiguously presented, standard specification sheets serve as check lists to ensure that all the information required is included.

Examples of equipment specification sheets are given in Appendix G.

### ***Process manuals***

Process manuals are often prepared by the process design group to describe the process and the basis of the design. Together with the flow-sheets, they provide a complete technical description of the process.

### ***Operating manuals***

Operating manuals give the detailed, step by step, instructions for operation of the process and equipment. They would normally be prepared by the operating company personnel, but may also be issued by a contractor as part of the contract package for a less experienced client. The operating manuals would be used for operator instruction and training, and for the preparation of the formal plant operating instructions.

## 1.6. CODES AND STANDARDS

The need for standardisation arose early in the evolution of the modern engineering industry; Whitworth introduced the first standard screw thread to give a measure of interchangeability between different manufacturers in 1841. Modern engineering standards cover a much wider function than the interchange of parts. In engineering practice they cover:

1. Materials, properties and compositions.
2. Testing procedures for performance, compositions, quality.
3. Preferred sizes; for example, tubes, plates, sections.
4. Design methods, inspection, fabrication.
5. Codes of practice, for plant operation and safety.

The terms STANDARD and CODE are used interchangeably, though CODE should really be reserved for a code of practice covering say, a recommended design or operating procedure; and STANDARD for preferred sizes, compositions, etc.

All of the developed countries, and many of the developing countries, have national standards organisations, responsible for the issue and maintenance of standards for the manufacturing industries, and for the protection of consumers. In the United Kingdom preparation and promulgation of national standards are the responsibility of the British Standards Institution (BSI). The Institution has a secretariat and a number of technical personnel, but the preparation of the standards is largely the responsibility of committees of persons from the appropriate industry, the professional engineering institutions and other interested organisations.

In the United States the government organisation responsible for coordinating information on standards is the National Bureau of Standards; standards are issued by Federal, State and various commercial organisations. The principal ones of interest to chemical engineers are those issued by the American National Standards Institute (ANSI), the American Petroleum Institute (API), the American Society for Testing Materials (ASTM), and the American Society of Mechanical Engineers (ASME) (pressure vessels). Burklin (1979) gives a comprehensive list of the American codes and standards.

The International Organization for Standardization (ISO) coordinates the publication of international standards.

All the published British standards are listed, and their scope and application described, in the *British Standards Institute Catalogue*; which the designer should consult. The catalogue is available online, go to the BSI group home page, [www.bsi-global.com](http://www.bsi-global.com).

As well as the various national standards and codes, the larger design organisations will have their own (in-house) standards. Much of the detail in engineering design work is routine and repetitious, and it saves time and money, and ensures a conformity between projects, if standard designs are used whenever practicable.

Equipment manufacturers also work to standards to produce standardised designs and size ranges for commonly used items; such as electric motors, pumps, pipes and pipe fittings. They will conform to national standards, where they exist, or to those issued by trade associations. It is clearly more economic to produce a limited range of standard sizes than to have to treat each order as a special job.

For the designer, the use of a standardised component size allows for the easy integration of a piece of equipment into the rest of the plant. For example, if a standard range of centrifugal pumps is specified the pump dimensions will be known, and this facilitates the design of the foundations plates, pipe connections and the selection of the drive motors: standard electric motors would be used.

For an operating company, the standardisation of equipment designs and sizes increases interchangeability and reduces the stock of spares that have to be held in maintenance stores.

Though there are clearly considerable advantages to be gained from the use of standards in design, there are also some disadvantages. Standards impose constraints on the designer. The nearest standard size will normally be selected on completing a design calculation (rounding-up) but this will not necessarily be the optimum size; though as the standard size will be cheaper than a special size, it will usually be the best choice from the point of view of initial capital cost. Standard design methods must, of their nature, be historical, and do not necessarily incorporate the latest techniques.

The use of standards in design is illustrated in the discussion of the pressure vessel design standards (codes) in Chapter 13.

## 1.7. FACTORS OF SAFETY (DESIGN FACTORS)

Design is an inexact art; errors and uncertainties will arise from uncertainties in the design data available and in the approximations necessary in design calculations. To ensure that the design specification is met, factors are included to give a margin of safety in the design; safety in the sense that the equipment will not fail to perform satisfactorily, and that it will operate safely: will not cause a hazard. "Design factor" is a better term to use, as it does not confuse safety and performance factors.

In mechanical and structural design, the magnitude of the design factors used to allow for uncertainties in material properties, design methods, fabrication and operating loads are well established. For example, a factor of around 4 on the tensile strength, or about 2.5 on the 0.1 per cent proof stress, is normally used in general structural design. The selection of design factors in mechanical engineering design is illustrated in the discussion of pressure vessel design in Chapter 13.

Design factors are also applied in process design to give some tolerance in the design. For example, the process stream average flows calculated from material balances are usually increased by a factor, typically 10 per cent, to give some flexibility in process operation. This factor will set the maximum flows for equipment, instrumentation, and piping design. Where design factors are introduced to give some contingency in a process design, they should be agreed within the project organisation, and clearly stated in the project documents (drawings, calculation sheets and manuals). If this is not done, there is a danger that each of the specialist design groups will add its own "factor of safety"; resulting in gross, and unnecessary, over-design.

When selecting the design factor to use a balance has to be made between the desire to make sure the design is adequate and the need to design to tight margins to remain competitive. The greater the uncertainty in the design methods and data, the bigger the design factor that must be used.

## 1.8. SYSTEMS OF UNITS

To be consistent with the other volumes in this series, SI units have been used in this book. However, in practice the design methods, data and standards which the designer will use are often only available in the traditional scientific and engineering units. Chemical engineering has always used a diversity of units; embracing the scientific CGS and MKS systems, and both the American and British engineering systems. Those engineers in the older industries will also have had to deal with some bizarre traditional units; such as degrees Twaddle (density) and barrels for quantity. Desirable as it may be for industry world-wide to adopt one consistent set of units, such as SI, this is unlikely to come about for many years, and the designer must contend with whatever system, or combination of systems, his organisation uses. For those in the contracting industry this will also mean working with whatever system of units the client requires.

It is usually the best practice to work through design calculations in the units in which the result is to be presented; but, if working in SI units is preferred, data can be converted to SI units, the calculation made, and the result converted to whatever units are required. Conversion factors to the SI system from most of the scientific and engineering units used in chemical engineering design are given in Appendix D.

Some license has been taken in the use of the SI system in this volume. Temperatures are given in degrees Celsius ( $^{\circ}\text{C}$ ); degrees Kelvin are only used when absolute temperature is required in the calculation. Pressures are often given in bar (or atmospheres) rather than in the Pascals ( $\text{N}/\text{m}^2$ ), as this gives a better feel for the magnitude of the pressures. In technical calculations the bar can be taken as equivalent to an atmosphere, whatever definition is used for atmosphere. The abbreviations bara and barg are often used to denote bar absolute and bar gauge; analogous to psia and psig when the pressure is expressed in pound force per square inch. When bar is used on its own, without qualification, it is normally taken as absolute.

For stress,  $\text{N}/\text{mm}^2$  have been used, as these units are now generally accepted by engineers, and the use of a small unit of area helps to indicate that stress is the intensity of force at a point (as is also pressure). For quantity, kmol are generally used in preference to mol, and for flow, kmol/h instead of mol/s, as this gives more sensibly sized figures, which are also closer to the more familiar lb/h.

For volume and volumetric flow,  $\text{m}^3$  and  $\text{m}^3/\text{h}$  are used in preference to  $\text{m}^3/\text{s}$ , which gives ridiculously small values in engineering calculations. Litres per second are used for small flow-rates, as this is the preferred unit for pump specifications.

Where, for convenience, other than SI units have been used on figures or diagrams, the scales are also given in SI units, or the appropriate conversion factors are given in the text. The answers to some examples are given in British engineering units as well as SI, to help illustrate the significance of the values.

Some approximate conversion factors to SI units are given in Table 1.1. These are worth committing to memory, to give some feel for the units for those more familiar with the traditional engineering units. The exact conversion factors are also shown in the table. A more comprehensive table of conversion factors is given in Appendix D.

Engineers need to be aware of the difference between US gallons and imperial gallons (UK) when using American literature and equipment catalogues. Equipment quoted in an

Table 1.1. Approximate conversion units

Quantity	British Eng. unit	SI unit approx.	exact
Energy	1 Btu	1 kJ	1.05506
Specific enthalpy	1 Btu/lb	2 kJ/kg	2.326
Specific heat capacity	1 Btu/lb <sup>o</sup> F (CHU/lb <sup>o</sup> C)	4 kJ/kg <sup>o</sup> C	4.1868
Heat transfer coeff.	1 Btu/ft <sup>2</sup> h <sup>o</sup> F (CHU/ft <sup>2</sup> h <sup>o</sup> C)	6 W/m <sup>2</sup> <sup>o</sup> C	5.678
Viscosity	1 centipoise	1 mNs/m <sup>2</sup>	1.000
	1 lb <sub>f</sub> /ft h	0.4 mNs/m <sup>2</sup>	0.4134
Surface tension	1 dyne/cm	1 mN/m	1.000
Pressure	1 lb <sub>f</sub> /in <sup>2</sup>	7 kN/m <sup>2</sup>	6.894
	1 atm	1 bar 10 <sup>5</sup> N/m <sup>2</sup>	1.01325
Density	1 lb/ft <sup>3</sup>	16 kg/m <sup>3</sup>	16.0190
	1 g/cm <sup>3</sup>	1 kg/m <sup>3</sup>	
Volume	1 imp gal.	4.5 × 10 <sup>-3</sup> m <sup>3</sup>	4.5461 × 10 <sup>-3</sup>
Flow-rate	1 imp gal/m	16 m <sup>3</sup> /h	16.366

Note:

1 US gallon = 0.84 imperial gallons (UK)

1 barrel (oil) = 50 US gall ≈ 0.19 m<sup>3</sup> (exact 0.1893)

1 kWh = 3.6 MJ

American catalogue in US gallons or gpm (gallons per minute) will have only 80 per cent of the rated capacity when measured in imperial gallons.

The electrical supply frequency in these two countries is also different: 60 Hz in the US and 50 Hz in the UK. So a pump specified as 50 gpm (US gallons), running at 1750 rpm (revolutions per second) in the US would only deliver 35 imp gpm if operated in the UK; where the motor speed would be reduced to 1460 rpm: so beware.

## 1.9. DEGREES OF FREEDOM AND DESIGN VARIABLES. THE MATHEMATICAL REPRESENTATION OF THE DESIGN PROBLEM

In Section 1.2 it was shown that the designer in seeking a solution to a design problem works within the constraints inherent in the particular problem.

In this section the structure of design problems is examined by representing the general design problem in a mathematical form.

### 1.9.1. Information flow and design variables

A process unit in a chemical process plant performs some operation on the inlet material streams to produce the desired outlet streams. In the design of such a unit the design calculations model the operation of the unit. A process unit and the design equations



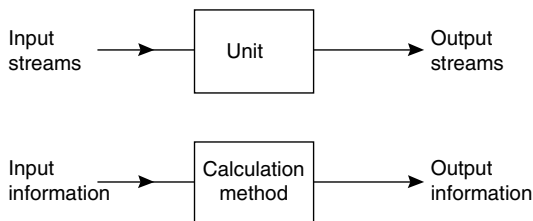


Figure 1.6. The “design unit”

representing the unit are shown diagrammatically in Figure 1.6. In the “design unit” the flow of material is replaced by a flow of information into the unit and a flow of derived information from the unit.

The information flows are the values of the variables which are involved in the design; such as, stream compositions, temperatures, pressure, stream flow-rates, and stream enthalpies. Composition, temperature and pressure are intensive variables: independent of the quantity of material (flow-rate). The constraints on the design will place restrictions on the possible values that these variables can take. The values of some of the variables will be fixed directly by process specifications. The values of other variables will be determined by “design relationships” arising from constraints. Some of the design relationships will be in the form of explicit mathematical equations (design equations); such as those arising from material and energy balances, thermodynamic relationships, and equipment performance parameters. Other relationships will be less precise; such as those arising from the use of standards and preferred sizes, and safety considerations.

The difference between the number of variables involved in a design and the number of design relationships has been called the number of “degrees of freedom”; similar to the use of the term in the phase rule. The number of variables in the system is analogous to the number of variables in a set of simultaneous equations, and the number of relationships analogous to the number of equations. The difference between the number of variables and equations is called the variance of the set of equations.

If  $N_v$  is the number of possible variables in a design problem and  $N_r$  the number of design relationships, then the “degrees of freedom”  $N_d$  is given by:

$$N_d = N_v - N_r \quad (1.1)$$

$N_d$  represents the freedom that the designer has to manipulate the variables to find the best design.

If  $N_v = N_r$ ,  $N_d = 0$  and there is only one, unique, solution to the problem. The problem is not a true design problem, no optimisation is possible.

If  $N_v < N_r$ ,  $N_d < 0$ , and the problem is over defined; only a trivial solution is possible.

If  $N_v > N_r$ ,  $N_d > 0$ , and there is an infinite number of possible solutions. However, for a practical problem there will be only a limited number of feasible solutions. The value of  $N_d$  is the number of variables which the designer must assign values to solve the problem.

How the number of process variables, design relationships, and design variables defines a system can be best illustrated by considering the simplest system; a single-phase, process stream.

### Process stream

Consider a single-phase stream, containing  $C$  components.

Variable	Number
Stream flow-rate	1
Composition (component concentrations)	$C$
Temperature	1
Pressure	1
Stream enthalpy	1
Total, $N_v = C + 4$	
Relationships between variables	Number
Composition <sup>(1)</sup>	1
Enthalpy <sup>(2)</sup>	1
Total, $N_r = 2$	

Degrees of freedom  $N_d = N_v - N_r = (C + 4) - 2 = \underline{\underline{C + 2}}$

- (1) The sum of the mass or mol, fractions, must equal one.  
 (2) The enthalpy is a function of stream composition, temperature and pressure.

Specifying  $(C + 2)$  variables completely defines the stream.

### Flash distillation

The idea of degrees of freedom in the design process can be further illustrated by considering a simple process unit, a flash distillation. (For a description of flash distillation see Volume 2, Chapter 11).

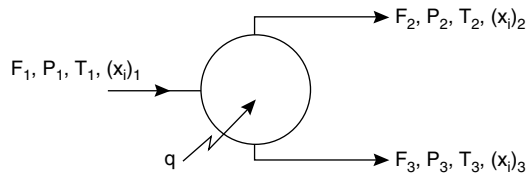


Figure 1.7. Flash distillation

The unit is shown in Figure 1.7, where:

$F$  = stream flow rate,

$P$  = pressure,

$T$  = temperature,

$x_i$  = concentration, component  $i$ ,

$q$  = heat input.

Suffixes, 1 = inlet, 2 = outlet vapour, 3 = outlet liquid.

Variable	Number
Streams (free variables) <sup>(1)</sup>	$3(C + 2)$ <sup>1</sup>
Still	
pressure	1
temperature	1
heat input	1
$N_r = 3C + 9$	
Relationship	Number
Material balances (each component)	$C$
Heat balance, overall	1
v-l-e relationships <sup>(2)</sup>	$C$
Equilibrium still restriction <sup>(3)</sup>	4
$2C + 5$	

$$\text{Degrees of freedom } N_d = (3C + 9) - (2C + 5) = \underline{\underline{C + 4}}$$

(1) The degrees of freedom for each stream. The total variables in each stream could have been used, and the stream relationships included in the count of relationships.

This shows how the degrees of freedom for a complex unit can be built up from the degrees of freedom of its components. For more complex examples see Kwauk (1956).

(2) Given the temperature and pressure, the concentration of any component in the vapour phase can be obtained from the concentration in the liquid phase, from the vapour-liquid equilibrium data for the system.

(3) The concept (definition) of an equilibrium separation implies that the outlet streams and the still are at the same temperature and pressure. This gives four equations:

$$P_2 = P_3 = P$$

$$T_2 = T_3 = T$$

Though the total degrees of freedom is seen to be  $(C + 4)$  some of the variables will normally be fixed by general process considerations, and will not be free for the designer to select as “design variables”. The flash distillation unit will normally be one unit in a process system and the feed composition and feed conditions will be fixed by the upstream processes; the feed will arise as an outlet stream from some other unit. Defining the feed fixes  $(C + 2)$  variables, so the designer is left with:

$$(C + 4) - (C + 2) = 2$$

as design variables.

### Summary

The purpose of this discussion was to show that in a design there will be a certain number of variables that the designer must specify to define the problem, and which he can manipulate to seek the best design. In manual calculations the designer will rarely

need to calculate the degrees of freedom in a formal way. He will usually have intuitive feel for the problem, and can change the calculation procedure, and select the design variables, as he works through the design. He will know by experience if the problem is correctly specified. A computer, however, has no intuition, and for computer-aided design calculations it is essential to ensure that the necessary number of variables is specified to define the problem correctly. For complex processes the number of variables and relating equations will be very large, and the calculation of the degrees of freedom very involved. Kwauk (1956) has shown how the degrees of freedom can be calculated for separation processes by building up the complex unit from simpler units. Smith (1963) uses Kwauk's method, and illustrates how the idea of "degrees of freedom" can be used in the design of separation processes.

### 1.9.2. Selection of design variables

In setting out to solve a design problem the designer has to decide which variables are to be chosen as "design variables"; the ones he will manipulate to produce the best design. The choice of design variables is important; careful selection can simplify the design calculations. This can be illustrated by considering the choice of design variables for a simple binary flash distillation.

For a flash distillation the total degrees of freedom was shown to be  $(C + 4)$ , so for two components  $N_d = 6$ . If the feed stream flow, composition, temperature and pressure are fixed by upstream conditions, then the number of design variables will be:

$$N'_d = 6 - (C + 2) = 6 - 4 = 2$$

So the designer is free to select two variables from the remaining variables in order to proceed with the calculation of the outlet stream compositions and flows.

If he selects the still pressure (which for a binary system will determine the vapour-liquid-equilibrium relationship) and one outlet stream flow-rate, then the outlet compositions can be calculated by simultaneous solution of the mass balance and equilibrium relationships (equations). A graphical method for the simultaneous solution is given in Volume 2, Chapter 11.

However, if he selects an outlet stream composition (say the liquid stream) instead of a flow-rate, then the simultaneous solution of the mass balance and v-l-e relationships would not be necessary. The stream compositions could be calculated by the following step-by-step (sequential) procedure:

1. Specifying  $P$  determines the v-l-e relationship (equilibrium) curve from experimental data.
2. Knowing the outlet liquid composition, the outlet vapour composition can be calculated from the v-l-e relationship.
3. Knowing the feed and outlet compositions, and the feed flow-rate, the outlet stream flows can be calculated from a material balance.
4. An enthalpy balance then gives the heat input required.

The need for simultaneous solution of the design equations implies that there is a recycle of information. Choice of an outlet stream composition as a design variable in

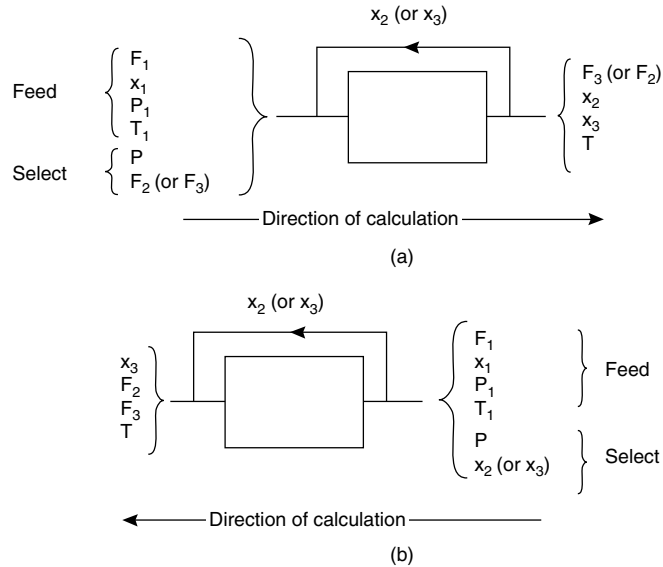


Figure 1.8. Information flow, binary flash distillation calculation (a) Information recycle (b) Information flow reversal

effect reverses the flow of information through the problem and removes the recycle; this is shown diagrammatically in Figure 1.8.

### 1.9.3. Information flow and the structure of design problems

It was shown in Section 1.9.2. by studying a relatively simple problem, that the way in which the designer selects his design variables can determine whether the design calculations will prove to be easy or difficult. Selection of one particular set of variables can lead to a straightforward, step-by-step, procedure, whereas selection of another set can force the need for simultaneous solution of some of the relationships; which often requires an iterative procedure (cut-and-try method). How the choice of design variables, inputs to the calculation procedure, affects the ease of solution for the general design problem can be illustrated by studying the flow of information, using simple information flow diagrams. The method used will be that given by Lee *et al.* (1966) who used a form of directed graph; a biparte graph, see Berge (1962).

The general design problem can be represented in mathematical symbolism as a series of equations:

$$f_i(v_j) = 0$$

where  $j = 1, 2, 3, \dots, N_v$ ,

$$i = 1, 2, 3, \dots, N_r$$

Consider the following set of such equations:

$$f_1(v_1, v_2) = 0$$

$$f_2(v_1, v_2, v_3, v_5) = 0$$

$$f_3(v_1, v_3, v_4) = 0$$

$$f_4(v_2, v_4, v_5, v_6) = 0$$

$$f_5(v_5, v_6, v_7) = 0$$

There are seven variables,  $N_v = 7$ , and five equations (relationships)  $N_r = 5$ , so the number of degrees of freedom is:

$$N_d = N_v - N_r = 7 - 5 = \underline{\underline{2}}$$

The task is to select two variables from the total of seven in such a way as to give the simplest, most efficient, method of solution to the seven equations. There are twenty-one ways of selecting two items from seven.

In Lee's method the equations and variables are represented by nodes on the biparte graph (circles), connected by edges (lines), as shown in Figure 1.9.

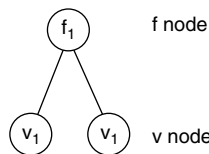


Figure 1.9. Nodes and edges on a biparte graph

Figure 1.9 shows that equation  $f_1$  contains (is connected to) variables  $v_1$  and  $v_2$ . The complete graph for the set of equations is shown in Figure 1.10.

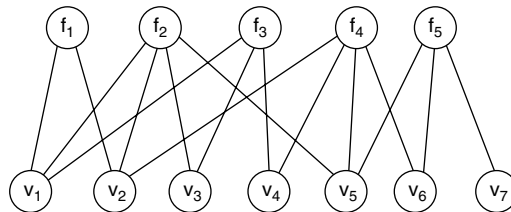


Figure 1.10. Biparte graph for the complete set of equations

The number of edges connected to a node defines the local degree of the node  $p$ . For example, the local degree of the  $f_1$  node is 2,  $p(f_1) = 2$ , and at the  $v_5$  node it is 3,  $p(v_5) = 3$ . Assigning directions to the edges of Figure 1.10 (by putting arrows on the lines) identifies one possible order of solution for the equations. If a variable  $v_j$  is defined as an output variable from an equation  $f_i$ , then the direction of information flow is from the node  $f_i$  to the node  $v_j$  and all other edges will be oriented into  $f_i$ . What this means, mathematically, is that assigning  $v_j$  as an output from  $f_i$  rearranges that equation so that:

$$f_i(v_1, v_2, \dots, v_n) = v_j$$

$v_j$  is calculated from equation  $f_i$ .

The variables selected as design variables (fixed by the designer) cannot therefore be assigned as output variables from an  $f$  node. They are inputs to the system and their edges must be oriented into the system of equations.

If, for instance, variables  $v_3$  and  $v_4$  are selected as design variables, then Figure 1.11 shows one possible order of solution of the set of equations. Different types of arrows are used to distinguish between input and output variables, and the variables selected as design variables are enclosed in a double circle.

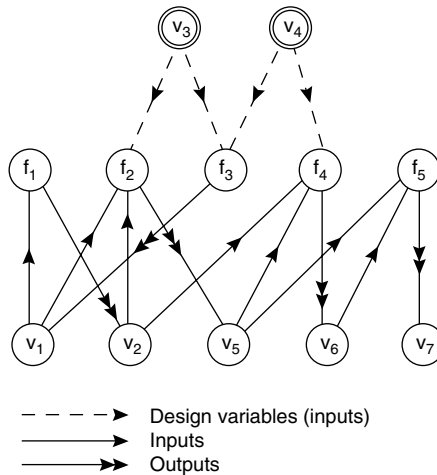


Figure 1.11. An order of solution

Tracing the order of the solution of the equations as shown in Figure 1.11 shows how the information flows through the system of equations:

1. Fixing  $v_3$  and  $v_4$  enables  $f_3$  to be solved, giving  $v_1$  as the output.  $v_1$  is an input to  $f_1$  and  $f_2$ .
2. With  $v_1$  as an input,  $f_1$  can be solved giving  $v_2$ ;  $v_2$  is an input to  $f_2$  and  $f_4$ .
3. Knowing  $v_3$ ,  $v_1$  and  $v_2$ ,  $f_2$  can be solved to give  $v_5$ ;  $v_5$  is an input to  $f_4$  and  $f_5$ .
4. Knowing  $v_4$ ,  $v_2$  and  $v_5$ ,  $f_4$  can be solved to give  $v_6$ ;  $v_6$  is an input to  $f_5$ .
5. Knowing  $v_6$  and  $v_5$ ,  $f_5$  can be solved to give  $v_7$ ; which completes the solution.

This order of calculation can be shown more clearly by redrawing Figure 1.11 as shown in Figure 1.12.

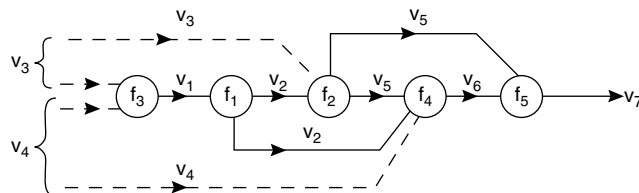


Figure 1.12. Figure 1.11 redrawn to show order of solution

With this order, the equations can be solved sequentially, with no need for the simultaneous solution of any of the equations. The fortuitous selection of  $v_3$  and  $v_4$  as design variables has given an efficient order of solution of the equations.

If for a set of equations an order of solution exists such that there is no need for the simultaneous solution of any of the equations, the system is said to be “acyclic”, no recycle of information.

If another pair of variables had been selected, for instance  $v_5$  and  $v_7$ , an acyclic order of solution for the set of equations would not necessarily have been obtained.

For many design calculations it will not be possible to select the design variables so as to eliminate the recycle of information and obviate the need for iterative solution of the design relationships.

For example, the set of equations given below will be cyclic for all choices of the two possible design variables.

$$\begin{aligned} f_1(x_1, x_2) &= 0 \\ f_2(x_1, x_3, x_4) &= 0 \\ f_3(x_2, x_3, x_4, x_5, x_6) &= 0 \\ f_4(x_4, x_5, x_6) &= 0 \\ N_d &= 6 - 4 = 2 \end{aligned}$$

The biparte graph for this example, with  $x_3$  and  $x_5$  selected as the design variables (inputs), is shown in Figure 1.13.

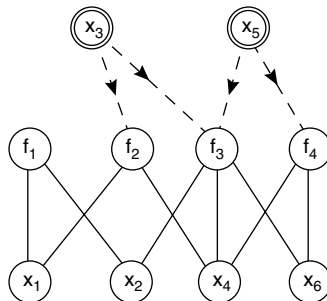


Figure 1.13.

One strategy for the solution of this cyclic set of equations would be to guess (assign a value to)  $x_6$ . The equations could then be solved sequentially, as shown in Figure 1.14, to produce a calculated value for  $x_6$ , which could be compared with the assumed value and the procedure repeated until a satisfactory convergence of the assumed and calculated value had been obtained. Assigning a value to  $x_6$  is equivalent to “tearing” the recycle loop at  $x_6$  (Figure 1.15). Iterative methods for the solution of equations are discussed by Henley and Rosen (1969).

When a design problem cannot be reduced to an acyclic form by judicious selection of the design variables, the design variables should be chosen so as to reduce the recycle of



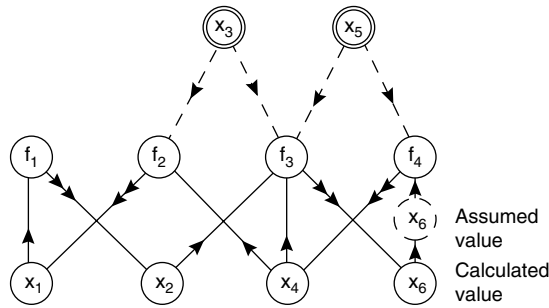


Figure 1.14.

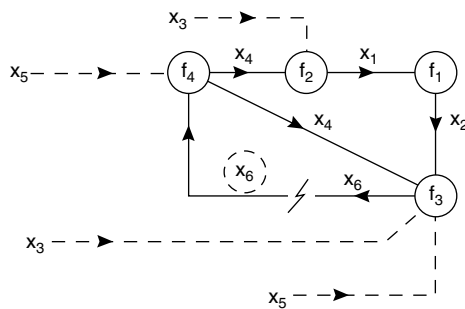


Figure 1.15.

information to a minimum. Lee and Rudd (1966) and Rudd and Watson (1968) give an algorithm that can be used to help in the selection of the best design variables in manual calculations.

The recycle of information, often associated with the actual recycle of process material, will usually occur in any design problem involving large sets of equations; such as in the computer simulation of chemical processes. Efficient methods for the solution of sets of equations are required in computer-aided design procedures to reduce the computer time needed. Several workers have published algorithms for the efficient ordering of recycle loops for iterative solution procedures, and some references to this work are given in the chapter on flow-sheeting, Chapter 4.

## 1.10. OPTIMISATION

Design is optimisation: the designer seeks the best, the optimum, solution to a problem.

Much of the selection and choice in the design process will depend on the intuitive judgement of the designer; who must decide when more formal optimisation techniques can be used to advantage.

The task of formally optimising the design of a complex processing plant involving several hundred variables, with complex interactions, is formidable, if not impossible. The task can be reduced by dividing the process into more manageable units, identifying the key variables and concentrating work where the effort involved will give the greatest

benefit. Sub-division, and optimisation of the sub-units rather than the whole, will not necessarily give the optimum design for the whole process. The optimisation of one unit may be at the expense of another. For example, it will usually be satisfactory to optimise the reflux ratio for a fractionating column independently of the rest of the plant; but if the column is part of a separation stage following a reactor, in which the product is separated from the unreacted materials, then the design of the column will interact with, and may well determine, the optimisation of the reactor design.

In this book the discussion of optimisation methods will, of necessity, be limited to a brief review of the main techniques used in process and equipment design. The extensive literature on the subject should be consulted for full details of the methods available, and their application and limitations; see Beightler and Wilde (1967), Beveridge and Schechter (1970), Stoecker (1989), Rudd and Watson (1968), Edgar and Himmelblau (2001). The books by Rudd and Watson (1968) and Edgar and Himmelblau (2001) are particularly recommended to students.

### **1.10.1. General procedure**

When setting out to optimise any system, the first step is clearly to identify the objective: the criterion to be used to judge the system performance. In engineering design the objective will invariably be an economic one. For a chemical process, the overall objective for the operating company will be to maximise profits. This will give rise to sub-objectives, which the designer will work to achieve. The main sub-objective will usually be to minimise operating costs. Other sub-objectives may be to reduce investment, maximise yield, reduce labour requirements, reduce maintenance, operate safely.

When choosing his objectives the designer must keep in mind the overall objective. Minimising cost per unit of production will not necessarily maximise profits per unit time; market factors, such as quality and delivery, may determine the best overall strategy.

The second step is to determine the objective function: the system of equations, and other relationships, which relate the objective with the variables to be manipulated to optimise the function. If the objective is economic, it will be necessary to express the objective function in economic terms (costs).

Difficulties will arise in expressing functions that depend on value judgements; for example, the social benefits and the social costs that arise from pollution.

The third step is to find the values of the variables that give the optimum value of the objective function (maximum or minimum). The best techniques to be used for this step will depend on the complexity of the system and on the particular mathematical model used to represent the system.

A mathematical model represents the design as a set of equations (relationships) and, as was shown in Section 1.9.1, it will only be possible to optimise the design if the number of variables exceeds the number of relationships; there is some degree of freedom in the system.

### **1.10.2. Simple models**

If the objective function can be expressed as a function of one variable (single degree of freedom) the function can be differentiated, or plotted, to find the maximum or minimum.

This will be possible for only a few practical design problems. The technique is illustrated in Example 1.1, and in the derivation of the formula for optimum pipe diameter in Chapter 5. The determination of the economic reflux ratio for a distillation column, which is discussed in Volume 2, Chapter 11, is an example of the use of a graphical procedure to find the optimum value.

### Example 1.1

The optimum proportions for a cylindrical container. A classical example of the optimisation of a simple function.

The surface area,  $A$ , of a closed cylinder is:

$$A = \pi \times D \times L + 2\frac{\pi}{4}D^2$$

where  $D$  = vessel diameter

$L$  = vessel length (or height)

This will be the objective function which is to be minimised; simplified:

$$f(D \times L) = D \times L + \frac{D^2}{2} \quad (\text{equation A})$$

For a given volume,  $V$ , the diameter and length are related by:

$$V = \frac{\pi}{4}D^2 \times L$$

and

$$L = \frac{4V}{\pi D^2} \quad (\text{equation B})$$

and the objective function becomes

$$f(D) = \frac{4V}{\pi D} + \frac{D^2}{2}$$

Setting the differential of this function zero will give the optimum value for  $D$

$$\frac{-4V}{\pi D^2} + D = 0$$

$$D = \sqrt[3]{\frac{4V}{\pi}}$$

From equation B, the corresponding length will be:

$$L = \sqrt[3]{\frac{4V}{\pi}}$$

So for a cylindrical container the minimum surface area to enclose a given volume is obtained when the length is made equal to the diameter.

In practice, when cost is taken as the objective function, the optimum will be nearer  $L = 2D$ ; the proportions of the ubiquitous tin can, and oil drum. This is because the cost

will include that of forming the vessel and making the joints, in addition to cost of the material (the surface area); see Wells (1973).

If the vessel is a pressure vessel the optimum length to diameter ratio will be even greater, as the thickness of plate required is a direct function of the diameter; see Chapter 13. Urbaniec (1986) gives procedures for the optimisation of tanks and vessel, and other process equipment.

### 1.10.3. Multiple variable problems

The general optimisation problem can be represented mathematically as:

$$f = f(v_1, v_2, v_3, \dots, v_n) \quad (1.2)$$

where  $f$  is the objective function and  $v_1, v_2, v_3, \dots, v_n$  are the variables.

In a design situation there will be constraints on the possible values of the objective function, arising from constraints on the variables; such as, minimum flow-rates, maximum allowable concentrations, and preferred sizes and standards.

Some may be equality constraints, expressed by equations of the form:

$$\Phi_m = \Phi_m(v_1, v_2, v_3, \dots, v_n) = 0 \quad (1.3)$$

Others as inequality constraints:

$$\Psi_p = \Psi_p(v_1, v_2, v_3, \dots, v_n) \leq P_p \quad (1.4)$$

The problem is to find values for the variables  $v_1$  to  $v_n$  that optimise the objective function: that give the maximum or minimum value, within the constraints.

### **Analytical methods**

If the objective function can be expressed as a mathematical function the classical methods of calculus can be used to find the maximum or minimum. Setting the partial derivatives to zero will produce a set of simultaneous equations that can be solved to find the optimum values. For the general, unconstrained, objective function, the derivatives will give the critical points; which may be maximum or minimum, or ridges or valleys. As with single variable functions, the nature of the first derivative can be found by taking the second derivative. For most practical design problems the range of values that the variables can take will be subject to constraints (equations 1.3 and 1.4), and the optimum of the constrained objective function will not necessarily occur where the partial derivatives of the objective function are zero. This situation is illustrated in Figure 1.16 for a two-dimensional problem. For this problem, the optimum will lie on the boundary defined by the constraint  $y = a$ .

The method of Lagrange's undetermined multipliers is a useful analytical technique for dealing with problems that have equality constraints (fixed design values). Examples of the use of this technique for simple design problems are given by Stoecker (1989), Peters and Timmerhaus (1991) and Boas (1963a).

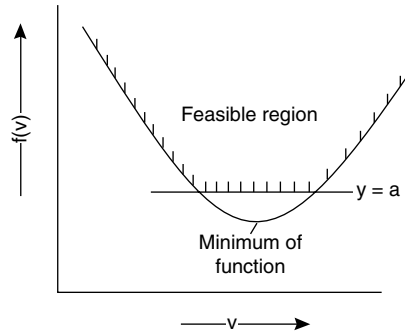


Figure 1.16. Effect of constraints on optimum of a function

### Search methods

The nature of the relationships and constraints in most design problems is such that the use of analytical methods is not feasible. In these circumstances search methods, that require only that the objective function can be computed from arbitrary values of the independent variables, are used. For single variable problems, where the objective function is unimodal, the simplest approach is to calculate the value of the objective function at uniformly spaced values of the variable until a maximum (or minimum) value is obtained. Though this method is not the most efficient, it will not require excessive computing time for simple problems. Several more efficient search techniques have been developed, such as the method of the golden section; see Boas (1963b) and Edgar and Himmelblau (2001).

Efficient search methods will be needed for multi-dimensional problems, as the number of calculations required and the computer time necessary will be greatly increased, compared with single variable problems; see Himmelblau (1963), Stoecker (1971), Beveridge and Schechter (1970), and Baasel (1974).

Two variable problems can be plotted as shown in Figure 1.17. The values of the objective function are shown as contour lines, as on a map, which are slices through the three-dimensional model of the function. Seeking the optimum of such a function can be

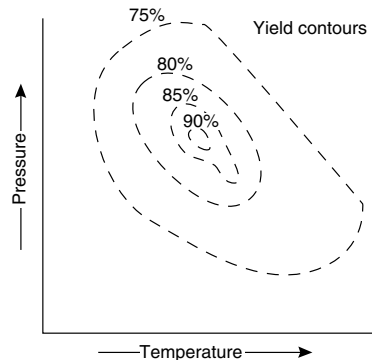


Figure 1.17. Yield as a function of reactor temperature and pressure

likened to seeking the top of a hill (or bottom of a valley), and a useful technique for this type of problem is the *gradient method* (*method of steepest ascent, or descent*), see Edgar and Himmelblau (2001).

#### 1.10.4. Linear programming

Linear programming is an optimisation technique that can be used when the objective function and constraints can be expressed as a linear function of the variables; see Driebeek (1969), Williams (1967) and Dano (1965).

The technique is useful where the problem is to decide the optimum utilisation of resources. Many oil companies use linear programming to determine the optimum schedule of products to be produced from the crude oils available. Algorithms have been developed for the efficient solution of linear programming problems and the SIMPLEX algorithm, Dantzig (1963), is the most commonly used.

Examples of the application of linear programming in chemical process plant design and operation are given by Allen (1971), Rudd and Watson (1968), Stoecker (1991), and Urbaniec (1986).

#### 1.10.5. Dynamic programming

Dynamic programming is a technique developed for the optimisation of large systems; see Nemhauser (1966), Bellman (1957) and Aris (1963).

The basic approach used is to divide the system into convenient sub-systems and optimise each sub-system separately, while taking into account the interactions between the sub-systems. The decisions made at each stage contribute to the overall systems objective function, and to optimise the overall objective function an appropriate combination of the individual stages has to be found. In a typical process plant system the possible number of combinations of the stage decisions will be very large. The dynamic programming approach uses Bellman's "Principle of Optimality",<sup>†</sup> which enables the optimum policy to be found systematically and efficiently by calculating only a fraction of the possible combinations of stage decisions. The method converts the problem from the need to deal with "*N*" optimisation decisions simultaneously to a sequential set of "*N*" problems. The application of dynamic programming to design problems is well illustrated in Rudd and Watson's book; see also Wells (1973) and Edgar and Himmelblau (2001).

#### 1.10.6. Optimisation of batch and semicontinuous processes

In batch operation there will be periods when product is being produced, followed by non-productive periods when the product is discharged and the equipment prepared for the next batch. The rate of production will be determined by the total batch time, productive

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<sup>†</sup> Bellman's (1957) principle of optimality: "An optimal policy has the property that, whatever the initial state and the initial decision are, the remaining decisions must constitute an optimal policy with regard to the state resulting from the first decision."

plus non-productive periods.

$$\text{Batches per year} = \frac{8760 \times \text{plant attainment}}{\text{batch cycle time}} \quad (1.5)$$

where the “plant attainment” is the fraction of the total hours in a year (8760) that the plant is in operation.

Annual production = quantity produced per batch  $\times$  batches per year.

$$\text{Cost per unit of production} = \frac{\text{annual cost of production}}{\text{annual production rate}} \quad (1.6)$$

With many batch processes, the production rate will decrease during the production period; for example, batch reactors and plate and frame filter presses, and there will be an optimum batch size, or optimum cycle time, that will give the minimum cost per unit of production.

For some processes, though they would not be classified as batch processes, the period of continuous production will be limited by gradual changes in process conditions; such as, the deactivation of catalysts or the fouling of heat-exchange surfaces. Production will be lost during the periods when the plant is shut down for catalyst renewal or equipment clean-up, and, as with batch process, there will be an optimum cycle time to give the minimum production cost.

The optimum time between shut-downs can be found by determining the relationship between cycle time and cost per unit of production (the objective function) and using one of the optimisation techniques outlined in this section to find the minimum.

With discontinuous processes, the period between shut-downs will usually be a function of equipment size. Increasing the size of critical equipment will extend the production period, but at the expense of increased capital cost. The designer must strike a balance between the savings gained by reducing the non-productive period and the increased investment required.

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## 1.12. NOMENCLATURE

		Dimensions in <b>MLT<math>\theta</math></b>
$C$	Number of components	—
$D$	Diameter	<b>L</b>
$F$	Stream flow rate	<b>MT<sup>-1</sup></b>
$f$	General function	—
$f_i$	General function (design relationship)	—
$f_1, f_2 \dots$	General functions (design relationships)	—
$L$	Length	<b>L</b>
$N_d$	Degrees of freedom in a design problem	—
$N'_d$	Degrees of freedom (variables free to be selected as design variables)	—
$N_r$	Number of design relationships	—
$N_v$	Number of variables	—
$P$	Pressure	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
$P_p$	Inequality constraints	—
$q$	Heat input, flash distillation	<b>ML<sup>2</sup>T<sup>-3</sup></b>
$T$	Temperature	<b><math>\theta</math></b>
$v_j$	Variables	—
$v_1, v_2 \dots$	Variables	—
$x_1, x_2 \dots$	Variables	—
$\Phi$	Equality constraint function	—
$\Psi$	Inequality constraint function	—
<i>Suffixes</i>		
1	Inlet, flash distillation	
2	Vapour outlet, flash distillation	
3	Liquid outlet, flash distillation	



### 1.13 PROBLEMS

- 1.1. Given that 1 in = 25.4 mm; 1 lbm = 0.4536 kg; 1 °F = 0.556 °C; 1 cal = 4.1868 J;  $g = 9.807 \text{ m s}^{-2}$ , calculate conversion factors to SI units for the following terms:
- i. feet
  - ii. pounds mass
  - iii. pounds force
  - iv. horse power (1 HP = 550 foot pounds per second)
  - v. psi (pounds per square inch)
  - vi.  $\text{lb ft}^{-1} \text{ s}^{-1}$  (viscosity)
  - vii. poise ( $\text{gm cm}^{-1} \text{ s}^{-1}$ )
  - viii. Btu (British Thermal Unit)
  - ix. CHU (Centigrade Heat Unit) also known as PCU (Pound Centigrade Unit)
  - x.  $\text{Btu ft}^{-2} \text{ h}^{-1} \text{ °F}^{-1}$  (heat transfer coefficient).
- 1.2. Determine the degrees of freedom available in the design of a simple heat exchanger. Take the exchanger as a double-pipe exchanger transferring heat between two single-phase streams.
- 1.3. A separator divides a process stream into three phases: a liquid organic stream, a liquid aqueous stream, and a gas stream. The feed stream contains three components, all of which are present to some extent in the separated streams. The composition and flowrate of the feed stream are known. All the streams will be at the same temperature and pressure. The phase equilibria for the three phases is available. How many design variables need to be specified in order to calculate the output stream compositions and flow rates?
- 1.4. A rectangular tank with a square base is constructed from 5 mm steel plates. If the capacity required is eight cubic metres determine the optimum dimensions if the tank has:
- i. a closed top
  - ii. an open top.
- 1.5. Estimate the optimum thickness of insulation for the roof of a house, given the following information. The insulation will be installed flat on the attic floor. Overall heat transfer coefficient for the insulation as a function of thickness,  $U$  values (see Chapter 12):
- |  |    |     |     |     |      |      |      |
|--|----|-----|-----|-----|------|------|------|
| thickness, mm                          | 0  | 25  | 50  | 100 | 150  | 200  | 250  |
| $U$ , $\text{Wm}^{-2} \text{ °C}^{-1}$ | 20 | 0.9 | 0.7 | 0.3 | 0.25 | 0.20 | 0.15 |
- Average temperature difference between inside and outside of house 10 °C; heating period 200 days in a year.  
 Cost of insulation, including installation, £70/m<sup>3</sup>. Capital charges (see Chapter 6) 15 per cent per year. Cost of fuel, allowing for the efficiency of the heating system, 6p/MJ.  
 Note: the rate at which heat is being lost is given by  $U \times \Delta T$ ,  $\text{W/m}^2$ , where  $U$  is the overall coefficient and  $\Delta T$  the temperature difference; see Chapter 12.

- 1.6.** (US version) Estimate the optimum thickness of insulation for the roof of a house given the following information. The insulation will be installed flat on the attic floor.

Overall heat transfer coefficient for the insulation as a function of thickness,  $U$  values (see Chapter 12):

thickness, mm	0	25	50	100	150	200	250
$U$ , $\text{Wm}^{-2} \text{ } ^\circ\text{C}^{-1}$	20	0.9	0.7	0.3	0.25	0.20	0.15

Average temperature difference between inside and outside of house  $12^\circ\text{C}$ ; heating period 250 days in a year. Cost of insulation, including installation,  $\$120/\text{m}^3$ . Capital charges (see chapter 6) 20 per cent per year. Cost of fuel, allowing for the efficiency of the heating system,  $9\text{c}/\text{MJ}$ .

Note: the rate at which heat is being lost is given by  $U \times \Delta T$ ,  $\text{W}/\text{m}^2$ , where  $U$  is the overall coefficient and  $\Delta T$  the temperature difference; see Chapter 12.

- 1.7.** What is the optimum practical shape for a dwelling, to minimise the heat losses through the building fabric?

Why is this optimum shape seldom used?

What people do use the optimum shape for their winter dwellings? Is heat retention their only consideration in their selection of this shape?

- 1.8.** You are part of the design team working on a project for the manufacture of cyclohexane.

The chief engineer calls you into his office and asks you to prepare an outline design for an inert gas purging and blanketing system for the reactors and other equipment, on shutdown. This request arises from a report into an explosion and fire at another site manufacturing a similar product.

Following the steps given in Figure 1.2, find what you consider the best solution to this design problem.

## CHAPTER 2

# *Fundamentals of Material Balances*

### 2.1. INTRODUCTION

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced. Balances over individual process units set the process stream flows and compositions.

A good understanding of material balance calculations is essential in process design.

In this chapter the fundamentals of the subject are covered, using simple examples to illustrate each topic. Practice is needed to develop expertise in handling what can often become very involved calculations. More examples and a more detailed discussion of the subject can be found in the numerous specialist books written on material and energy balance computations. Several suitable texts are listed under the heading of “Further Reading” at the end of this chapter.

The application of material balances to more complex problems is discussed in “Flow-sheeting”, Chapter 4.

Material balances are also useful tools for the study of plant operation and trouble shooting. They can be used to check performance against design; to extend the often limited data available from the plant instrumentation; to check instrument calibrations; and to locate sources of material loss.

### 2.2. THE EQUIVALENCE OF MASS AND ENERGY

Einstein showed that mass and energy are equivalent. Energy can be converted into mass, and mass into energy. They are related by Einstein’s equation:

$$E = mc^2 \quad (2.1)$$

where  $E$  = energy, J,

$m$  = mass, kg,

$c$  = the speed of light *in vacuo*,  $3 \times 10^8$  m/s.

The loss of mass associated with the production of energy is significant only in nuclear reactions. Energy and matter are always considered to be separately conserved in chemical reactions.

### 2.3. CONSERVATION OF MASS

The general conservation equation for any process system can be written as:

$$\text{Material out} = \text{Material in} + \text{Generation} - \text{Consumption} - \text{Accumulation}$$

For a steady-state process the accumulation term will be zero. Except in nuclear processes, mass is neither generated nor consumed; but if a chemical reaction takes place a particular chemical species may be formed or consumed in the process. If there is no chemical reaction the steady-state balance reduces to

$$\text{Material out} = \text{Material in}$$

A balance equation can be written for each separately identifiable species present, elements, compounds or radicals; and for the total material.

### Example 2.1

2000 kg of a 5 per cent slurry of calcium hydroxide in water is to be prepared by diluting a 20 per cent slurry. Calculate the quantities required. The percentages are by weight.

### Solution

Let the unknown quantities of the 20% slurry and water be  $X$  and  $Y$  respectively.

Material balance on  $\text{Ca}(\text{OH})_2$

$$\begin{array}{ccc} \textit{In} & & \textit{Out} \\ X \frac{20}{100} & = & 2000 \times \frac{5}{100} \end{array} \quad (a)$$

Balance on water

$$X \frac{(100 - 20)}{100} + Y = 2000 \frac{(100 - 5)}{100} \quad (b)$$

From equation (a)  $X = 500$  kg.

Substituting into equation (b) gives  $Y = \underline{\underline{1500}}$  kg

Check material balance on total quantity:

$$X + Y = 2000$$

$$500 + 1500 = 2000, \text{ correct}$$

## 2.4. UNITS USED TO EXPRESS COMPOSITIONS

When specifying a composition as a percentage it is important to state clearly the basis: weight, molar or volume.

The abbreviations w/w and v/v are used to designate weight basis and volume basis.

### Example 2.2

Technical grade hydrochloric acid has a strength of 28 per cent w/w, express this as a mol fraction.

**Solution**

Basis of calculation 100 kg of 28 per cent w/w acid.

Molecular mass: water 18, HCl 36.5

$$\text{Mass HCl} = 100 \times 0.28 = 28 \text{ kg}$$

$$\text{Mass water} = 100 \times 0.72 = 72 \text{ kg}$$

$$\text{kmol HCl} = \frac{28}{36.5} = 0.77$$

$$\text{kmol water} = \frac{72}{18} = 4.00$$

$$\text{Total mols} = 4.77$$

$$\text{mol fraction HCl} = \frac{0.77}{4.77} = 0.16$$

$$\text{mol fraction water} = \frac{4.00}{4.77} = 0.84$$

$$\text{Check total} = 1.00$$

Within the accuracy needed for technical calculations, volume fractions can be taken as equivalent to mol fractions for gases, up to moderate pressures (say 25 bar).

Trace quantities are often expressed as parts per million (ppm). The basis, weight or volume, needs to be stated.

$$\text{ppm} = \frac{\text{quantity of component}}{\text{total quantity}} \times 10^6$$

*Note.* 1 ppm =  $10^{-4}$  per cent.

Minute quantities are sometimes quoted in ppb, parts per billion. Care is needed here, as the billion is usually an American billion ( $10^9$ ), not the UK billion ( $10^{12}$ ).

**2.5. STOICHIOMETRY**

Stoichiometry (from the Greek *stoikeion*—element) is the practical application of the law of multiple proportions. The stoichiometric equation for a chemical reaction states unambiguously the number of molecules of the reactants and products that take part; from which the quantities can be calculated. The equation must balance.

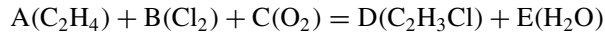
With simple reactions it is usually possible to balance the stoichiometric equation by inspection, or by trial and error calculations. If difficulty is experienced in balancing complex equations, the problem can always be solved by writing a balance for each element present. The procedure is illustrated in Example 2.3.

**Example 2.3**

Write out and balance the overall equation for the manufacture of vinyl chloride from ethylene, chlorine and oxygen.

**Solution**

*Method:* write out the equation using letters for the unknown number of molecules of each reactant and product. Make a balance on each element. Solve the resulting set of equations.



Balance on carbon

$$2A = 2D, \quad A = D$$

on hydrogen

$$4A = 3D + 2E$$

$$\text{substituting } D = A \text{ gives } E = \frac{A}{2}$$

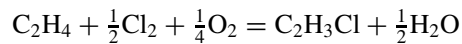
on chlorine

$$2B = D, \text{ hence } B = \frac{A}{2}$$

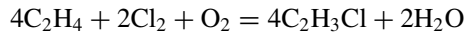
on oxygen

$$2C = E, \quad C = \frac{E}{2} = \frac{A}{4}$$

putting  $A = 1$ , the equation becomes



multiplying through by the largest denominator to remove the fractions

**2.6. CHOICE OF SYSTEM BOUNDARY**

The conservation law holds for the complete process and any sub-division of the process. The system boundary defines the part of the process being considered. The flows into and out of the system are those crossing the boundary and must balance with material generated or consumed within the boundary.

Any process can be divided up in an arbitrary way to facilitate the material balance calculations. The judicious choice of the system boundaries can often greatly simplify what would otherwise be difficult and tortuous calculations.

No hard and fast rules can be given on the selection of suitable boundaries for all types of material balance problems. Selection of the best sub-division for any particular process is a matter of judgement, and depends on insight into the structure of the problem, which can only be gained by practice. The following general rules will serve as a guide:

1. With complex processes, first take the boundary round the complete process and if possible calculate the flows in and out. Raw materials in, products and by-products out.
2. Select the boundaries to sub-divide the process into simple stages and make a balance over each stage separately.
3. Select the boundary round any stage so as to reduce the number of unknown streams to as few as possible.

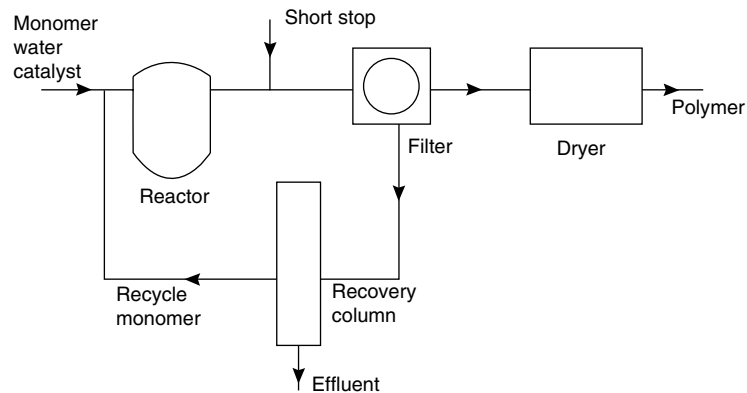
4. As a first step, include any recycle streams within the system boundary (see Section 2.14).

### Example 2.4

Selection of system boundaries and organisation of the solution.

The diagram shows the main steps in a process for producing a polymer. From the following data, calculate the stream flows for a production rate of 10,000 kg/h.

- Reactor, yield on polymer 100 per cent
- slurry polymerisation 20 per cent monomer/water conversion 90 per cent
- catalyst 1 kg/1000 kg monomer
- short stopping agent 0.5 kg/1000 kg unreacted monomer
- Filter, wash water approx. 1 kg/1 kg polymer
- Recovery column, yield 98 per cent (percentage recovered)
- Dryer, feed ~5 per cent water, product specification 0.5 per cent H<sub>2</sub>O
- Polymer losses in filter and dryer ~1 per cent

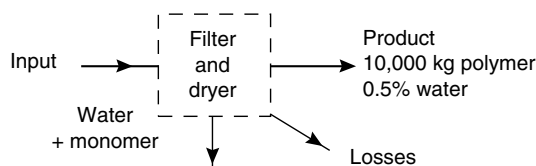


### Solution

Only those flows necessary to illustrate the choice of system boundaries and method of calculation are given in the Solution.

Basis: 1 hour

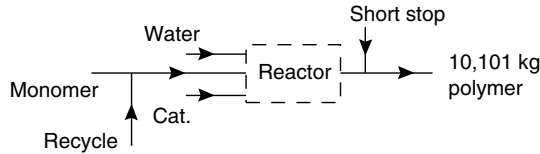
Take the first system boundary round the filter and dryer.



With 1 per cent loss, polymer entering sub-system

$$= \frac{10,000}{0.99} = \underline{\underline{10,101 \text{ kg}}}$$

Take the next boundary round the reactor system; the feeds to the reactor can then be calculated.



At 90 per cent conversion, monomer feed

$$= \frac{10,101}{0.9} = \underline{\underline{11,223 \text{ kg}}}$$

Unreacted monomer =  $11,223 - 10,101 = \underline{\underline{1122 \text{ kg}}}$

Short-stop, at 0.5 kg/1000 kg unreacted monomer

$$= 1122 \times 0.5 \times 10^{-3} = \underline{\underline{0.6 \text{ kg}}}$$

Catalyst, at 1 kg/1000 kg monomer

$$= 11,223 \times 1 \times 10^{-3} = \underline{\underline{11 \text{ kg}}}$$

Let water feed to reactor be  $F_1$ , then for 20 per cent monomer

$$0.2 = \frac{11,223}{F_1 + 11,223}$$

$$F_1 = \frac{11,223(1 - 0.2)}{0.2} = \underline{\underline{44,892 \text{ kg}}}$$

Now consider filter-dryer sub-system again.

Water in polymer to dryer, at 5 per cent (neglecting polymer loss)

$$= 10,101 \times 0.05 = \underline{\underline{505 \text{ kg}}}$$

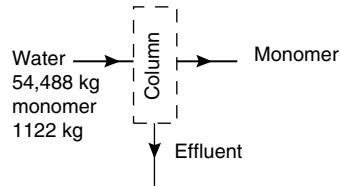
Balance over reactor-filter-dryer sub-system gives flows to recovery column.

water,  $44,892 + 10,101 - 505 = \underline{\underline{54,448 \text{ kg}}}$

monomer, unreacted monomer, =  $\underline{\underline{1122 \text{ kg}}}$



Now consider recovery system

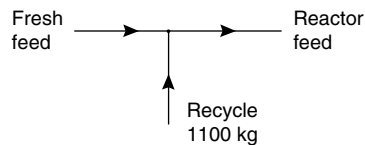


With 98 per cent recovery, recycle to reactor

$$= 0.98 \times 1122 = \underline{\underline{1100 \text{ kg}}}$$

Composition of effluent 23 kg monomer, 54,488 kg water.

Consider reactor monomer feed



Balance round tee gives fresh monomer required

$$= 11,223 - 1100 = \underline{\underline{10,123 \text{ kg}}}$$

## 2.7. CHOICE OF BASIS FOR CALCULATIONS

The correct choice of the basis for a calculation will often determine whether the calculation proves to be simple or complex. As with the choice of system boundaries, no all-embracing rules or procedures can be given for the selection of the right basis for any problem. The selection depends on judgement gained by experience. Some guide rules that will help in the choice are:

1. Time: choose the time basis in which the results are to be presented; for example kg/h, tonne/y.
2. For batch processes use one batch.
3. Choose as the mass basis the stream flow for which most information is given.
4. It is often easier to work in mols, rather than weight, even when no reaction is involved.
5. For gases, if the compositions are given by volume, use a volume basis, remembering that volume fractions are equivalent to mol fractions up to moderate pressures.

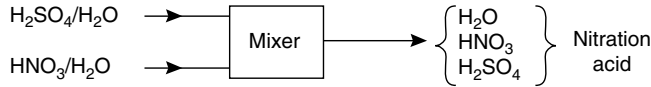
## 2.8. NUMBER OF INDEPENDENT COMPONENTS

A balance equation can be written for each independent component. Not all the components in a material balance will be independent.

**Physical systems, no reaction**

If there is no chemical reaction the number of independent components is equal to the number of distinct chemical species present.

Consider the production of a nitration acid by mixing 70 per cent nitric and 98 per cent sulphuric acid. The number of distinct chemical species is 3; water, sulphuric acid, nitric acid.



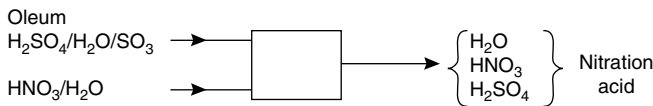
**Chemical systems, reaction**

If the process involves chemical reaction the number of independent components will not necessarily be equal to the number of chemical species, as some may be related by the chemical equation. In this situation the number of independent components can be calculated by the following relationship:

$$\text{Number of independent components} = \text{Number of chemical species} - \text{Number of independent chemical equations} \tag{2.2}$$

**Example 2.5**

If nitration acid is made up using oleum in place of the 98 per cent sulphuric acid, there will be four distinct chemical species: sulphuric acid, sulphur trioxide, nitric acid, water. The sulphur trioxide will react with the water producing sulphuric acid so there are only three independent components



No. of chemical species	4
No. of reactions	1
No. of independent equations	3

**2.9. CONSTRAINTS ON FLOWS AND COMPOSITIONS**

It is obvious, but worth emphasising, that the sum of the individual component flows in any stream cannot exceed the total stream flow. Also, that the sum of the individual molar or weight fractions must equal 1. Hence, the composition of a stream is completely defined if all but one of the component concentrations are given.

The component flows in a stream (or the quantities in a batch) are completely defined by any of the following:

1. Specifying the flow (or quantity) of each component.
2. Specifying the total flow (or quantity) and the composition.
3. Specifying the flow (or quantity) of one component and the composition.

### Example 2.6

The feed stream to a reactor contains: ethylene 16 per cent, oxygen 9 per cent, nitrogen 31 per cent, and hydrogen chloride. If the ethylene flow is 5000 kg/h, calculate the individual component flows and the total stream flow. All percentages are by weight.

### Solution

$$\text{Percentage HCl} = 100 - (16 + 9 + 31) = \underline{\underline{44}}$$

$$\text{Percentage ethylene} = \frac{5000}{\text{total}} \times 100 = \underline{\underline{16}}$$

$$\text{hence total flow} = 5000 \times \frac{100}{16} = \underline{\underline{31,250 \text{ kg/h}}}$$

$$\text{so, oxygen flow} = \frac{9}{100} \times 31,250 = \underline{\underline{2813 \text{ kg/h}}}$$

$$\text{nitrogen} = 31,250 \times \frac{31}{100} = \underline{\underline{9687 \text{ kg/h}}}$$

$$\text{hydrogen chloride} = 31,250 \times \frac{44}{100} = \underline{\underline{13,750 \text{ kg/h}}}$$

*General rule:* the ratio of the flow of any component to the flow of any other component is the same as the ratio of the compositions of the two components.

The flow of any component in Example 2.6 could have been calculated directly from the ratio of the percentage to that of ethylene, and the ethylene flow.

$$\text{Flow of hydrogen chloride} = \frac{44}{16} \times 5000 = \underline{\underline{13,750 \text{ kg/h}}}$$

## 2.10. GENERAL ALGEBRAIC METHOD

Simple material-balance problems involving only a few streams and with a few unknowns can usually be solved by simple direct methods. The relationship between the unknown quantities and the information given can usually be clearly seen. For more complex problems, and for problems with several processing steps, a more formal algebraic approach can be used. The procedure is involved, and often tedious if the calculations have to be done manually, but should result in a solution to even the most intractable problems, providing sufficient information is known.

Algebraic symbols are assigned to all the unknown flows and compositions. Balance equations are then written around each sub-system for the independent components (chemical species or elements).

Material-balance problems are particular examples of the general design problem discussed in Chapter 1. The unknowns are compositions or flows, and the relating equations arise from the conservation law and the stoichiometry of the reactions. For any problem to have a unique solution it must be possible to write the same number of independent equations as there are unknowns.

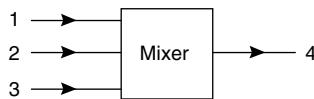
Consider the general material balance problem where there are  $N_s$  streams each containing  $N_c$  independent components. Then the number of variables,  $N_v$ , is given by:

$$N_v = N_c \times N_s \tag{2.3}$$

If  $N_e$  independent balance equations can be written, then the number of variables,  $N_d$ , that must be specified for a unique solution, is given by:

$$N_d = (N_s \times N_c) - N_e \tag{2.4}$$

Consider a simple mixing problem



Let  $F_n$  be the total flow in stream  $n$ , and  $x_{n,m}$  the concentration of component  $m$  in stream  $n$ . Then the general balance equation can be written

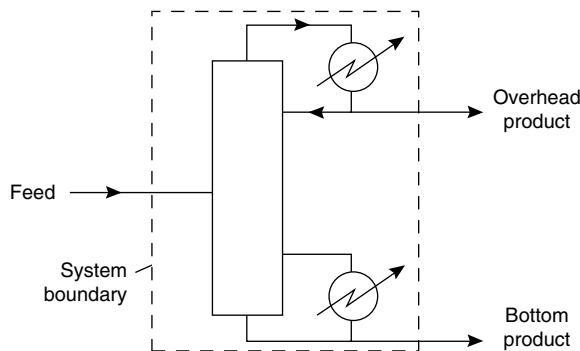
$$F_1x_{1,m} + F_2x_{2,m} + F_3x_{3,m} = F_4x_{4,m} \tag{2.5}$$

A balance equation can also be written for the total of each stream:

$$F_1 + F_2 + F_3 = F_4 \tag{2.6}$$

but this could be obtained by adding the individual component equations, and so is not an additional independent equation. There are  $m$  independent equations, the number of independent components.

Consider a separation unit, such as a distillation column, which divides a process stream into two product streams. Let the feed rate be 10,000 kg/h; composition benzene 60 per cent, toluene 30 per cent, xylene 10 per cent.



There are three streams, feed, overheads and bottoms, and three independent components in each stream.

$$\begin{aligned} \text{Number of variables (component flow rates)} &= 9 \\ \text{Number of independent material balance} \\ \text{equations} &= 3 \\ \text{Number of variables to be specified for} \\ \text{a unique solution} &= 9 - 3 = 6 \end{aligned}$$

Three variables are specified; the feed flow and composition fixes the flow of each component in the feed.

Number of variables to be specified by designer =  $6 - 3 = 3$ . Any three component flows can be chosen.

Normally the top composition and flow or the bottom composition and flow would be chosen.

If the primary function of the column is to separate the benzene from the other components, the maximum toluene and xylene in the overheads would be specified; say, at 5 kg/h and 3 kg/h, and the loss of benzene in the bottoms also specified; say, at not greater than 5 kg/h. Three flows are specified, so the other flows can be calculated.

Benzene in overheads = benzene in feed – benzene in bottoms.

$$0.6 \times 10,000 - 5 = \underline{\underline{5995 \text{ kg/h}}}$$

Toluene in bottoms = toluene in feed – toluene in overheads

$$0.3 \times 10,000 - 5 = \underline{\underline{2995 \text{ kg/h}}}$$

Xylene in bottoms = xylene in feed – xylene in overheads

$$0.1 \times 10,000 - 3 = \underline{\underline{997 \text{ kg/h}}}$$

## 2.11. TIE COMPONENTS

In Section 2.9 it was shown that the flow of any component was in the same ratio to the flow of any other component, as the ratio of the concentrations of the two components. If one component passes unchanged through a process unit it can be used to tie the inlet and outlet compositions.

This technique is particularly useful in handling combustion calculations where the nitrogen in the combustion air passes through unreacted and is used as the tie component. This is illustrated in Example 2.8.

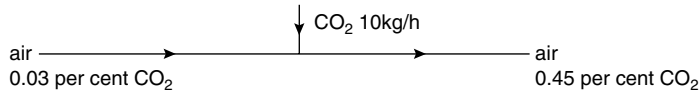
This principle can also be used to measure the flow of a process stream by introducing a measured flow of some easily analysed (compatible) material.

### Example 2.7

Carbon dioxide is added at a rate of 10 kg/h to an air stream and the air is sampled at a sufficient distance downstream to ensure complete mixing. If the analysis shows 0.45 per cent v/v CO<sub>2</sub>, calculate the air-flow rate.

**Solution**

Normal carbon dioxide content of air is 0.03 per cent



Basis: kmol/h, as percentages are by volume.

$$\text{kmol/h CO}_2 \text{ introduced} = \frac{10}{44} = 0.2273$$

Let  $X$  be the air flow.

Balance on  $\text{CO}_2$ , the tie component

$$\begin{aligned} \text{CO}_2 \text{ in} &= 0.0003 X + 0.2273 \\ \text{CO}_2 \text{ out} &= 0.0045 X \\ X(0.0045 - 0.0003) &= 0.2273 \\ X = 0.2273/0.0042 &= 54 \text{ kmol/h} \\ &= 54 \times \underline{29} = \underline{\underline{1560 \text{ kg/h}}} \end{aligned}$$

**Example 2.8**

In a test on a furnace fired with natural gas (composition 95 per cent methane, 5 per cent nitrogen) the following flue gas analysis was obtained: carbon dioxide 9.1 per cent, carbon monoxide 0.2 per cent, oxygen 4.6 per cent, nitrogen 86.1 per cent, all percentages by volume.

Calculate the percentage excess air flow (percentage above stoichiometric).

**Solution**

*Note:* the flue gas analysis is reported on the dry basis, any water formed having been condensed out.

Nitrogen is the tie component.

Basis: 100 mol, dry flue gas; as the analysis of the flue gas is known, the mols of each element in the flue gas (flow out) can be easily calculated and related to the flow into the system.

Let the quantity of fuel (natural gas) per 100 mol dry flue gas be  $X$ .

Balance on carbon, mols in fuel = mols in flue gas

$$0.95 X = 9.1 + 0.2, \text{ hence } X = \underline{\underline{9.79 \text{ mol}}}$$

Balance on nitrogen (composition of air  $\text{O}_2$  21 per cent,  $\text{N}_2$  79 per cent).

Let  $Y$  be the flow of air per 100 mol dry flue gas.

$\text{N}_2$  in air +  $\text{N}_2$  in fuel =  $\text{N}_2$  in flue gas

$$0.79 Y + 0.05 \times 9.79 = 86.1, \text{ hence } Y = \underline{\underline{108.4 \text{ mol}}}$$

Stoichiometric air; from the reaction equation 1 mol methane requires 2 mol oxygen,

$$\text{so, stoichiometric air} = 9.79 \times 0.95 \times 2 \times \frac{100}{21} = \underline{\underline{88.6 \text{ mol}}}$$

$$\begin{aligned} \text{Percentage excess air} &= \frac{(\text{air supplied} - \text{stoichiometric air})}{\text{stoichiometric air}} \times 100 \\ &= \frac{108.4 - 88.6}{88.6} = \underline{\underline{22 \text{ per cent}}} \end{aligned}$$

## 2.12. EXCESS REAGENT

In industrial reactions the components are seldom fed to the reactor in exact stoichiometric proportions. A reagent may be supplied in excess to promote the desired reaction; to maximise the use of an expensive reagent; or to ensure complete reaction of a reagent, as in combustion.

The percentage excess reagent is defined by the following equation:

$$\text{Per cent excess} = \frac{\text{quantity supplied} - \text{stoichiometric}}{\text{stoichiometric quantity}} \times 100 \quad (2.7)$$

It is necessary to state clearly to which reagent the excess refers. This is often termed the limiting reagent.

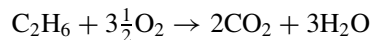
### Example 2.9

To ensure complete combustion, 20 per cent excess air is supplied to a furnace burning natural gas. The gas composition (by volume) is methane 95 per cent, ethane 5 per cent.

Calculate the mols of air required per mol of fuel.

### Solution

Basis: 100 mol gas, as the analysis is volume percentage.



$$\text{Stoichiometric mols O}_2 \text{ required} = 95 \times 2 + 5 \times 3\frac{1}{2} = \underline{\underline{207.5}}$$

$$\text{With 20 per cent excess, mols O}_2 \text{ required} = 207.5 \times \frac{120}{100} = \underline{\underline{249}}$$

$$\text{Mols air (21 per cent O}_2) = 249 \times \frac{100}{21} = 1185.7$$

$$\text{Air per mol fuel} = \frac{1185.7}{100} = \underline{\underline{11.86 \text{ mol}}}$$

## 2.13. CONVERSION AND YIELD

It is important to distinguish between conversion and yield (see Volume 3, Chapter 1). Conversion is to do with reactants (reagents); yield with products.

### Conversion

Conversion is a measure of the fraction of the reagent that reacts.

To optimise reactor design and to minimise by-product formation, the conversion of a particular reagent is often less than 100 per cent. If more than one reactant is used, the reagent on which the conversion is based must be specified.

Conversion is defined by the following expression:

$$\begin{aligned} \text{Conversion} &= \frac{\text{amount of reagent consumed}}{\text{amount supplied}} \\ &= \frac{(\text{amount in feed stream}) - (\text{amount in product stream})}{(\text{amount in feed stream})} \end{aligned} \quad (2.8)$$

This definition gives the total conversion of the particular reagent to all products. Sometimes figures given for conversion refer to one specific product, usually the desired product. In this instance the product must be specified as well as the reagent. This is really a way of expressing yield.

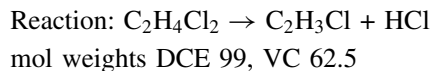
### Example 2.10

In the manufacture of vinyl chloride (VC) by the pyrolysis of dichloroethane (DCE), the reactor conversion is limited to 55 per cent to reduce carbon formation, which fouls the reactor tubes.

Calculate the quantity of DCE needed to produce 5000 kg/h VC.

### Solution

Basis: 5000 kg/h VC (the required quantity).



$$\text{kmol/h VC produced} = \frac{5000}{62.5} = \underline{\underline{80}}$$

From the stoichiometric equation, 1 kmol DCE produces 1 kmol VC. Let  $X$  be DCE feed kmol/h:

$$\begin{aligned} \text{Per cent conversion} &= 55 = \frac{80}{X} \times 100 \\ X &= \frac{80}{0.55} = \underline{\underline{145.5 \text{ kmol/h}}} \end{aligned}$$



In this example the small loss of DCE to carbon and other products has been neglected. All the DCE reacted has been assumed to be converted to VC.

### **Yield**

Yield is a measure of the performance of a reactor or plant. Several different definitions of yield are used, and it is important to state clearly the basis of any yield figures. This is often not done when yield figures are quoted in the literature, and the judgement has to be used to decide what was intended.

For a reactor the yield (i.e. *relative yield*, Volume 3, Chapter 1) is defined by:

$$\text{Yield} = \frac{\text{mols of product produced} \times \text{stoichiometric factor}}{\text{mols of reagent converted}} \quad (2.9)$$

Stoichiometric factor = Stoichiometric mols of reagent required per mol  
of product produced

With industrial reactors it is necessary to distinguish between “Reaction yield” (chemical yield), which includes only chemical losses to side products; and the overall “Reactor yield” which will include physical losses.

If the conversion is near 100 per cent it may not be worth separating and recycling the unreacted material; the overall reactor yield would then include the loss of unreacted material. If the unreacted material is separated and recycled, the overall yield *taken over the reactor and separation step* would include any physical losses from the separation step.

Plant yield is a measure of the overall performance of the plant and includes all chemical and physical losses.

Plant yield (applied to the complete plant or any stage)

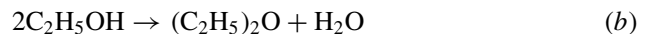
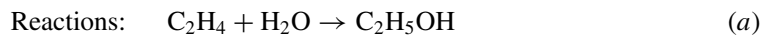
$$= \frac{\text{mols product produced} \times \text{stoichiometric factor}}{\text{mols reagent fed to the process}} \quad (2.10)$$

Where more than one reagent is used, or product produced, it is essential that product and reagent to which the yield figure refers is clearly stated.

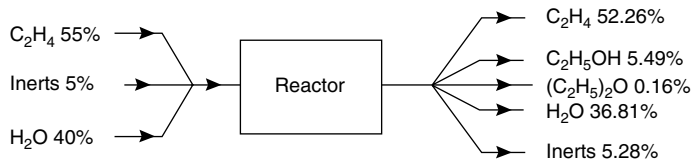
### **Example 2.11**

In the production of ethanol by the hydrolysis of ethylene, diethyl ether is produced as a by-product. A typical feed stream composition is: 55 per cent ethylene, 5 per cent inerts, 40 per cent water; and product stream: 52.26 per cent ethylene, 5.49 per cent ethanol, 0.16 per cent ether, 36.81 per cent water, 5.28 per cent inerts. Calculate the yield of ethanol and ether based on ethylene.

### **Solution**



Basis: 100 mols feed (easier calculation than using the product stream)



*Note:* the flow of inerts will be constant as they do not react, and it can be used to calculate the other flows from the compositions.

Feed stream	ethylene	55 mol
	inerts	5 mol
	water	40 mol

Product stream

$$\text{ethylene} = \frac{52.26}{5.28} \times 5 = 49.49 \text{ mol}$$

$$\text{ethanol} = \frac{5.49}{5.28} \times 5 = 5.20 \text{ mol}$$

$$\text{ether} = \frac{0.16}{5.28} \times 5 = 0.15 \text{ mol}$$

$$\text{Amount of ethylene reacted} = 55.0 - 49.49 = 5.51 \text{ mol}$$

$$\text{Yield of ethanol based on ethylene} = \frac{5.2 \times 1}{5.51} \times 100 = \underline{\underline{94.4 \text{ per cent}}}$$

As 1 mol of ethanol is produced per mol of ethylene the stoichiometric factor is 1.

$$\text{Yield of ether based on ethylene} = \frac{0.15 \times 2}{5.51} \times 100 = \underline{\underline{5.44 \text{ per cent}}}$$

The stoichiometric factor is 2, as 2 mol of ethylene produce 1 mol of ether.

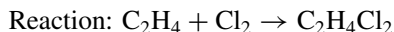
*Note:* the conversion of ethylene, to all products, is given by:

$$\begin{aligned} \text{Conversion} &= \frac{\text{mols fed} - \text{mols out}}{\text{mols fed}} = \frac{55 - 49.49}{55} \times 100 \\ &= \underline{\underline{10 \text{ per cent}}} \end{aligned}$$

The yield based on water could also be calculated but is of no real interest as water is relatively inexpensive compared with ethylene. Water is clearly fed to the reactor in considerable excess.

### Example 2.12

In the chlorination of ethylene to produce dichloroethane (DCE), the conversion of ethylene is reported as 99.0 per cent. If 94 mol of DCE are produced per 100 mol of ethylene fed, calculate the overall yield and the reactor (reaction) yield based on ethylene. The unreacted ethylene is not recovered.

**Solution**

Stoichiometric factor 1.

$$\begin{aligned} \text{Overall yield (including physical losses)} &= \frac{\text{mols DCE produced} \times 1}{\text{mols ethylene fed}} \times 100 \\ &= \frac{94}{100} \times 100 = \underline{\underline{94 \text{ per cent}}} \end{aligned}$$

$$\begin{aligned} \text{Chemical yield (reaction yield)} &= \frac{\text{mols DCE produced}}{\text{mols ethylene converted}} \times 100 \\ &= \frac{94}{99} \times 100 = \underline{\underline{94.5 \text{ per cent}}} \end{aligned}$$

The principal by-product of this process is trichloroethane.

**2.14. RECYCLE PROCESSES**

Processes in which a flow stream is returned (recycled) to an earlier stage in the processing sequence are frequently used. If the conversion of a valuable reagent in a reaction process is appreciably less than 100 per cent, the unreacted material is usually separated and recycled. The return of reflux to the top of a distillation column is an example of a recycle process in which there is no reaction.

In mass balance calculations the presence of recycle streams makes the calculations more difficult.

Without recycle, the material balances on a series of processing steps can be carried out sequentially, taking each unit in turn; the calculated flows out of one unit become the feeds to the next. If a recycle stream is present, then at the point where the recycle is returned the flow will not be known as it will depend on downstream flows not yet calculated. Without knowing the recycle flow, the sequence of calculations cannot be continued to the point where the recycle flow can be determined.

Two approaches to the solution of recycle problems are possible:

1. The cut and try method. The recycle stream flows can be estimated and the calculations continued to the point where the recycle is calculated. The estimated flows are then compared with the calculated and a better estimate made. The procedure is continued until the difference between the estimated and the calculated flows is within acceptable limits.
2. The formal, algebraic, method. The presence of recycle implies that some of the mass balance equations will have to be solved simultaneously. The equations are set up with the recycle flows as unknowns and solved using standard methods for the solution of simultaneous equations.

With simple problems, with only one or two recycle loops, the calculation can often be simplified by the careful selection of the basis of calculation and the system boundaries. This is illustrated in Examples 2.4 and 2.13.

The solution of more complex material balance problems involving several recycle loops is discussed in Chapter 4.

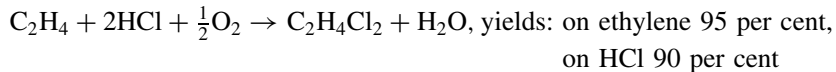
### Example 2.13

The block diagram shows the main steps in the balanced process for the production of vinyl chloride from ethylene. Each block represents a reactor and several other processing units. The main reactions are:

*Block A*, chlorination



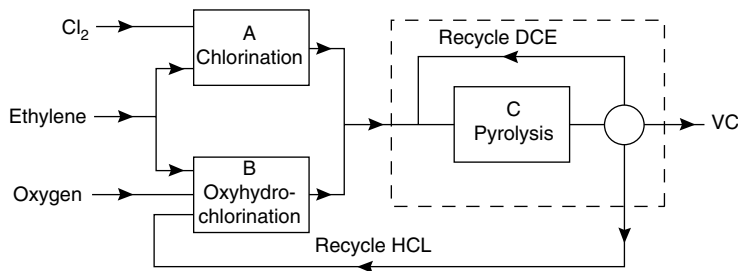
*Block B*, oxyhydrochlorination



*Block C*, pyrolysis



The HCl from the pyrolysis step is recycled to the oxyhydrochlorination step. The flow of ethylene to the chlorination and oxyhydrochlorination reactors is adjusted so that the production of HCl is in balance with the requirement. The conversion in the pyrolysis reactor is limited to 55 per cent, and the unreacted dichloroethane (DCE) separated and recycled.



Using the yield figures given, and neglecting any other losses, calculate the flow of ethylene to each reactor and the flow of DCE to the pyrolysis reactor, for a production rate of 12,500 kg/h vinyl chloride (VC).

### Solution

Molecular weights: vinyl chloride 62.5, DCE 99.0, HCl 36.5.

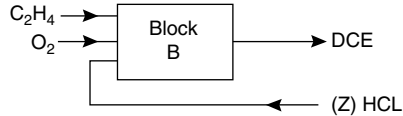
$$\text{VC per hour} = \frac{12,500}{62.5} = 200 \text{ kmol/h}$$

Draw a system boundary round each block, enclosing the DCE recycle within the boundary of step C.

Let flow of ethylene to block A be  $X$  and to block B be  $Y$ , and the HCl recycle be  $Z$ .  
Then the total mols of DCE produced =  $0.98X + 0.95Y$ , allowing for the yields, and the mols of HCl produced in block C

$$= (0.98X + 0.95Y)0.995 = Z \quad (a)$$

Consider the flows to and product from block B



The yield of DCE based on HCl is 90 per cent, so the mols of DCE produced

$$= \frac{0.90Z}{2}$$

*Note:* the stoichiometric factor is 2 (2 mol HCl per mol DCE).

The yield of DCE based on ethylene is 95 per cent, so

$$\frac{0.9Z}{2} = 0.95Y$$

$$Z = \frac{0.95 \times 2Y}{0.9}$$

Substituting for  $Z$  into equation (a) gives

$$Y = (0.98X + 0.95Y)0.995 \times \frac{0.9}{2 \times 0.95}$$

$$Y = 0.837X \quad (b)$$

Total VC produced =  $0.99 \times$  total DCE, so

$$0.99(0.98X + 0.95Y) = 200 \text{ kmol/h}$$

Substituting for  $Y$  from equation (b) gives  $X = \underline{\underline{113.8 \text{ kmol/h}}}$

and  $Y = 0.837 \times 113.8 = \underline{\underline{95.3 \text{ kmol/h}}}$

HCl recycle from equation (a)

$$Z = (0.98 \times 113.8 + 0.95 \times 95.3)0.995 = \underline{\underline{201.1 \text{ kmol/h}}}$$

$$\textit{Note: overall yield on ethylene} = \frac{200}{(113.8 + 95.3)} \times 100 = \underline{\underline{96 \text{ per cent}}}$$

## 2.15. PURGE

It is usually necessary to bleed off a portion of a recycle stream to prevent the build-up of unwanted material. For example, if a reactor feed contains inert components that are not

separated from the recycle stream in the separation units these inerts would accumulate in the recycle stream until the stream eventually consisted entirely of inerts. Some portion of the stream would have to be purged to keep the inert level within acceptable limits. A continuous purge would normally be used. Under steady-state conditions:

Loss of inert in the purge = Rate of feed of inerts into the system

The concentration of any component in the purge stream will be the same as that in the recycle stream at the point where the purge is taken off. So the required purge rate can be determined from the following relationship:

$$[\text{Feed stream flow-rate}] \times [\text{Feed stream inert concentration}] = [\text{Purge stream flow-rate}] \times [\text{Specified (desired) recycle inert concentration}]$$

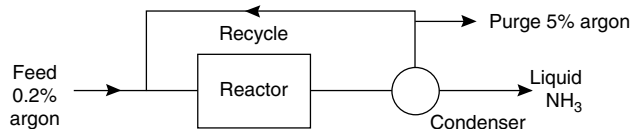
### Example 2.14

In the production of ammonia from hydrogen and nitrogen the conversion, based on either raw material, is limited to 15 per cent. The ammonia produced is condensed from the reactor (converter) product stream and the unreacted material recycled. If the feed contains 0.2 per cent argon (from the nitrogen separation process), calculate the purge rate required to hold the argon in the recycle stream below 5.0 per cent. Percentages are by volume.

### Solution

Basis: 100 mols feed (purge rate will be expressed as mols per 100 mol feed, as the production rate is not given).

Process diagram



Volume percentages are taken as equivalent to mol per cent.

Argon entering system with feed =  $100 \times 0.2/100 = 0.2$  mol.

Let purge rate per 100 mol feed be  $F$ .

Argon leaving system in purge =  $F \times 5/100 = 0.05F$ .

At the steady state, argon leaving = argon entering

$$0.05F = 0.2$$

$$F = \frac{0.2}{0.05} = \underline{\underline{4}}$$

Purge required: 4 mol per 100 mol feed.

### 2.16. BY-PASS

A flow stream may be divided and some part diverted (by-passed) around some units. This procedure is often used to control stream composition or temperature.

Material balance calculations on processes with by-pass streams are similar to those involving recycle, except that the stream is fed forward instead of backward. This usually makes the calculations easier than with recycle.

## 2.17. UNSTEADY-STATE CALCULATIONS

All the previous material balance examples have been steady-state balances. The accumulation term was taken as zero, and the stream flow-rates and compositions did not vary with time. If these conditions are not met the calculations are more complex. Steady-state calculations are usually sufficient for the calculations of the process flow-sheet (Chapter 4). The unsteady-state behaviour of a process is important when considering the process start-up and shut-down, and the response to process upsets.

Batch processes are also examples of unsteady-state operation; though the total material requirements can be calculated by taking one batch as the basis for the calculation.

The procedure for the solution of unsteady-state balances is to set up balances over a small increment of time, which will give a series of differential equations describing the process. For simple problems these equations can be solved analytically. For more complex problems computer methods would be used.

The general approach to the solution of unsteady-state problems is illustrated in Example 2.15. Batch distillation is a further example of an unsteady-state material balance (see Volume 2, Chapter 11).

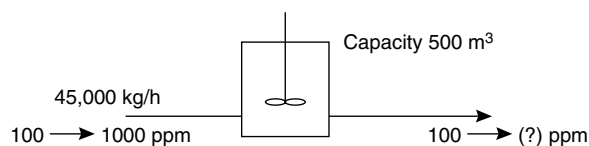
The behaviour of processes under non-steady-state conditions is a complex and specialised subject and beyond the scope of this book. It can be important in process design when assessing the behaviour of a process from the point of view of safety and control.

The use of material balances in the modelling of complex unsteady-state processes is discussed in the books by Myers and Seider (1976) and Henley and Rosen (1969).

### Example 2.15

A hold tank is installed in an aqueous effluent-treatment process to smooth out fluctuations in concentration in the effluent stream. The effluent feed to the tank normally contains no more than 100 ppm of acetone. The maximum allowable concentration of acetone in the effluent discharge is set at 200 ppm. The surge tank working capacity is 500 m<sup>3</sup> and it can be considered to be perfectly mixed. The effluent flow is 45,000 kg/h. If the acetone concentration in the feed suddenly rises to 1000 ppm, due to a spill in the process plant, and stays at that level for half an hour, will the limit of 200 ppm in the effluent discharge be exceeded?

### Solution



Basis: increment of time  $\Delta t$ .

To illustrate the general solution to this type of problem, the balance will be set up in terms of symbols for all the quantities and then actual values for this example substituted.

Let, Material in the tank =  $M$ ,

Flow-rate =  $F$ ,

Initial concentration in the tank =  $C_0$ ,

Concentration at time  $t$  after the feed concentration is increased =  $C$ ,

Concentration in the effluent feed =  $C_1$ ,

Change in concentration over time increment  $\Delta t = \Delta C$ ,

Average concentration in the tank during the time increment =  $C_{av}$ .

Then, as there is no generation in the system, the general material balance (Section 2.3) becomes:

$$\text{Input} - \text{Output} = \text{Accumulation}$$

Material balance on acetone.

*Note:* as the tank is considered to be perfectly mixed the outlet concentration will be the same as the concentration in the tank.

Acetone in – Acetone out = Acetone accumulated in the tank

$$FC_1\Delta t - FC_{av}\Delta t = M(C + \Delta C) - MC$$

$$F(C_1 - C_{av}) = M \frac{\Delta C}{\Delta t}$$

Taking the limit, as  $\Delta t \rightarrow 0$

$$\frac{\Delta C}{\Delta t} = \frac{dC}{dt}, \quad C_{av} = C$$

$$F(C_1 - C) = M \frac{dC}{dt}$$

Integrating

$$\int_0^t dt = \frac{M}{F} \int_{C_0}^C \frac{dC}{(C_1 - C)}$$

$$t = -\frac{M}{F} \ln \left[ \frac{C_1 - C}{C_1 - C_0} \right]$$

Substituting the values for the example, noting that the maximum outlet concentration will occur at the end of the half-hour period of high inlet concentration.

$$t = 0.5 \text{ h}$$

$$C_1 = 1000 \text{ ppm}$$

$$C_0 = 100 \text{ ppm (normal value)}$$

$$M = 500 \text{ m}^3 = 500,000 \text{ kg}$$

$$F = 45,000 \text{ kg/h}$$



$$0.5 = -\frac{500,000}{45,000} \ln \left[ \frac{1000 - C}{1000 - 100} \right]$$

$$0.045 = -\ln \left[ \frac{1000 - C}{900} \right]$$

$$e^{-0.045} \times 900 = 1000 - C$$

$$C = \underline{\underline{140 \text{ ppm}}}$$

So the maximum allowable concentration will not be exceeded.

## 2.18. GENERAL PROCEDURE FOR MATERIAL-BALANCE PROBLEMS

The best way to tackle a problem will depend on the information given; the information required from the balance; and the constraints that arise from the nature of the problem. No all embracing, best method of solution can be given to cover all possible problems. The following step-by-step procedure is given as an aid to the efficient solution of material balance problems. The same general approach can be usefully employed to organise the solution of energy balance, and other design problems.

### ***Procedure***

- Step 1. Draw a block diagram of the process.  
Show each significant step as a block, linked by lines and arrows to show the stream connections and flow direction.
- Step 2. List all the available data.  
Show on the block diagram the known flows (or quantities) and stream compositions.
- Step 3. List all the information required from the balance.
- Step 4. Decide the system boundaries (see Section 2.6).
- Step 5. Write out all the chemical reactions involved for the main products and by-products.
- Step 6. Note any other constraints,  
such as: specified stream compositions,  
azeotropes,  
phase equilibria,  
tie substances (see Section 2.11).

The use of phase equilibrium relationships and other constraints in determining stream compositions and flows is discussed in more detail in Chapter 4.

- Step 7. Note any stream compositions and flows that can be approximated.
- Step 8. Check the number of conservation (and other) equations that can be written, and compare with the number of unknowns. Decide which variables are to be design variables; see Section 2.10.  
This step would be used only for complex problems.

Step 9. Decide the basis of the calculation; see Section 2.7.

The order in which the steps are taken may be varied to suit the problem.

## 2.19. REFERENCES (FURTHER READING)

### Basic texts

- CHOPEY, N. P. (ed.) *Handbook of Chemical Engineering Calculations* (McGraw-Hill, 1984).  
 FELDER, R. M. and ROUSSEAU, R. W. *Elementary Principles of Chemical Processes*, 6th edn (Pearson, 1995).  
 HIMMELBLAU, D. M. *Basic Principles and Calculations in Chemical Engineering* (Prentice-Hall, 1982).  
 RUDD, D. F., POWERS, G. J. and SHIROLA, J. J. *Process Synthesis* (Prentice-Hall, 1973).  
 WHITWELL, J. C. and TONER, R. K. *Conservation of Mass and Energy* (McGraw-Hill, 1969).  
 WILLIAMS, E. T. and JACKSON, R. C. *Stoichiometry for Chemical Engineers* (McGraw-Hill, 1958).

### Advanced texts

- HENLEY, E. J. and ROSEN, E. M. (1969) *Material and Energy Balance Computations* (Wiley).  
 MYERS, A. L. and SEIDER, W. D. (1976) *Introduction to Chemical Engineering and Computer Calculations* (Prentice-Hall).

## 2.20. NOMENCLATURE

	Dimensions in MLT	
$C$	Concentration after time $t$ , Example 2.15	—
$C_{av}$	Average concentration, Example 2.15	—
$C_0$	Initial concentration, Example 2.15	—
$C_1$	Concentration in feed to tank, Example 2.15	—
$\Delta C$	Incremental change in concentration, Example 2.15	—
$F$	Flow-rate	$MT^{-1}$
$F_n$	Total flow in stream $n$	$MT^{-1}$
$F_1$	Water feed to reactor, Example 2.4	$MT^{-1}$
$M$	Quantity in hold tank, Example 2.15	$M$
$N_c$	Number of independent components	—
$N_d$	Number of variables to be specified	—
$N_e$	Number of independent balance equations	—
$N_s$	Number of streams	—
$N_v$	Number of variables	—
$t$	Time, Example 2.15	$T$
$\Delta t$	Incremental change in time, Example 2.15	$T$
$X$	Unknown flow, Examples 2.8, 2.10, 2.13	$MT^{-1}$
$x_{n,m}$	Concentration of component $m$ in stream $n$	—
$Y$	Unknown flow, Examples 2.8, 2.13	$MT^{-1}$
$Z$	Unknown flow, Example 2.13	$MT^{-1}$

## 2.21. PROBLEMS

**2.1.** The composition of a gas derived by the gasification of coal is, volume percentage: carbon dioxide 4, carbon monoxide 16, hydrogen 50, methane 15, ethane 3, benzene 2, balance nitrogen. If the gas is burnt in a furnace with 20 per cent excess air, calculate:

- the amount of air required per 100 kmol of gas,
- The amount of flue gas produced per 100 kmol of gas,

(c) the composition of the flue gases, on a dry basis.

Assume complete combustion.

**2.2.** Ammonia is removed from a stream of air by absorption in water in a packed column. The air entering the column is at 760 mmHg pressure and 20 °C. The air contains 5.0 per cent v/v ammonia. Only ammonia is absorbed in the column. If the flow rate of the ammonia air mixture to the column is 200 m<sup>3</sup>/s and the stream leaving the column contains 0.05 per cent v/v ammonia, calculate:

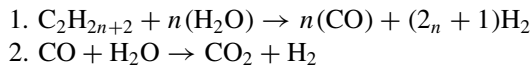
- The flow-rate of gas leaving the column.
- The mass of ammonia absorbed.
- The flow-rate of water to the column, if the exit water contains 1% w/w ammonia.

**2.3.** The off-gases from a gasoline stabiliser are fed to a reforming plant to produce hydrogen.

The composition of the off-gas, molar per cent, is: CH<sub>4</sub> 77.5, C<sub>2</sub>H<sub>6</sub> 9.5, C<sub>3</sub>H<sub>8</sub> 8.5, C<sub>4</sub>H<sub>10</sub> 4.5.

The gases entering the reformer are at a pressure of 2 bara and 35 °C and the feed rate is 2000 m<sup>3</sup>/h.

The reactions in the reformer are:



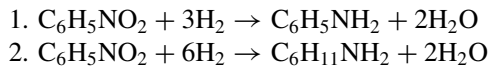
The molar conversion of C<sub>2</sub>H<sub>2n+2</sub> in reaction (1) is 96 per cent and of CO in reaction (2) 92 per cent.

Calculate:

- the average molecular mass of the off-gas,
- the mass of gas fed to the reformer, kg/h,
- the mass of hydrogen produced, kg/h.

**2.4.** Allyl alcohol can be produced by the hydrolysis of allyl chloride. Together with the main product, allyl alcohol, di-allyl ether is produced as a by-product. The conversion of allyl chloride is typically 97 per cent and the yield to alcohol 90 per cent, both on a molar basis. Assuming that there are no other significant side reactions, calculate masses of alcohol and ether produced, per 1000 kg of allyl chloride fed to the reactor.

**2.5.** Aniline is produced by the hydrogenation of nitrobenzene. A small amount of cyclo-hexylamine is produced as a by-product. The reactions are:



Nitrobenzene is fed to the reactor as a vapour, with three times the stoichiometric quantity of hydrogen. The conversion of the nitrobenzene, to all products, is 96 per cent, and the yield to aniline 95 per cent.

The unreacted hydrogen is separated from the reactor products and recycled to the reactor. A purge is taken from the recycle stream to maintain the inerts in the

recycle stream below 5 per cent. The fresh hydrogen feed is 99.5 per cent pure, the remainder being inerts. All percentages are molar.

For a feed rate of 100 kmol/h of nitrobenzene, calculate:

- (a) the fresh hydrogen feed,
- (b) the purge rate required,
- (c) the composition of the reactor outlet stream.

**2.6.** In the manufacture of aniline by the hydrogenation of nitrobenzene, the off-gases from the reactor are cooled and the products and unreacted nitrobenzene condensed. The hydrogen and inerts, containing only traces of the condensed materials, are recycled.

Using the typical composition of the reactor off-gas given below, estimate the stream compositions leaving the condenser.

Composition, kmol/h: aniline 950, cyclo-hexylamine 10, water 1920, hydrogen 5640, nitrobenzene 40, inerts 300.

**2.7.** In the manufacture of aniline, the condensed reactor products are separated in a decanter. The decanter separates the feed into an organic phase and an aqueous phase. Most of the aniline in the feed is contained in the organic phase and most of the water in the aqueous phase. Using the data given below, calculate the stream compositions.

Data:

Typical feed composition, including impurities and by-products, weight per cent: water 23.8, aniline 72.2, nitrobenzene 3.2, cyclo-hexylamine 0.8.

Density of aqueous layer 0.995, density of organic layer 1.006. Therefore, the organic layer will be at the bottom.

Solubility of aniline in water 3.2 per cent w/w, and water in aniline 5.15 per cent w/w.

Partition coefficient of nitrobenzene between the aqueous and organic phases:

$$C_{\text{organic}}/C_{\text{water}} = 300$$

Solubility of cyclo-hexylamine in the water phase 0.12 per cent w/w and in the organic phase 1.0 per cent w/w.

**2.8.** In the manufacture of aniline from nitrobenzene the reactor products are condensed and separated into an aqueous and organic phases in a decanter. The organic phase is fed to a stripping column to recover the aniline. Aniline and water form an azeotrope, composition 0.96 mol fraction aniline. For the feed composition given below, make a mass balance round the column and determine the stream compositions and flow-rates. Take as the basis for the balance 100 kg/h feed and a 99.9 percentage recovery of the aniline in the overhead product. Assume that the nitrobenzene leaves with the water stream from the base of the column.

Feed composition, weight percentage: water 2.4, aniline 73.0, nitrobenzene 3.2, cyclo-hexylamine trace.

---

Note: Problems 2.5 to 2.8 can be taken together as an exercise in the calculation of a preliminary material balance for the manufacture of aniline by the process described in detail in Appendix F, Problem F.8.

## CHAPTER 3

# *Fundamentals of Energy Balances (and Energy Utilisation)*

### 3.1. INTRODUCTION

As with mass, energy can be considered to be separately conserved in all but nuclear processes.

The conservation of energy, however, differs from that of mass in that energy can be generated (or consumed) in a chemical process. Material can change form, new molecular species can be formed by chemical reaction, but the total mass flow into a process unit must be equal to the flow out at the steady state. The same is not true of energy. The total enthalpy of the outlet streams will not equal that of the inlet streams if energy is generated or consumed in the processes; such as that due to heat of reaction.

Energy can exist in several forms: heat, mechanical energy, electrical energy, and it is the total energy that is conserved.

In process design, energy balances are made to determine the energy requirements of the process: the heating, cooling and power required. In plant operation, an energy balance (energy audit) on the plant will show the pattern of energy usage, and suggest areas for conservation and savings.

In this chapter the fundamentals of energy balances are reviewed briefly, and examples given to illustrate the use of energy balances in process design. The methods used for energy recovery and conservation are also discussed.

More detailed accounts of the principles and applications of energy balances are given in the texts covering material and energy balance calculations which are cited at the end of Chapter 2.

### 3.2. CONSERVATION OF ENERGY

As for material (Section 2.3), a general equation can be written for the conservation of energy:

$$\text{Energy out} = \text{Energy in} + \text{generation} - \text{consumption} - \text{accumulation}$$

This is a statement of the first law of thermodynamics.

An energy balance can be written for any process step.

Chemical reaction will evolve energy (exothermic) or consume energy (endothermic).

For steady-state processes the accumulation of both mass and energy will be zero.

Energy can exist in many forms and this, to some extent, makes an energy balance more complex than a material balance.

### 3.3. FORMS OF ENERGY (PER UNIT MASS OF MATERIAL)

#### 3.3.1. Potential energy

Energy due to position:

$$\text{Potential energy} = gz \quad (3.1)$$

where  $z$  = height above some arbitrary datum, m,

$g$  = gravitational acceleration (9.81 m/s<sup>2</sup>).

#### 3.3.2. Kinetic energy

Energy due to motion:

$$\text{Kinetic energy} = \frac{u^2}{2} \quad (3.2)$$

where  $u$  = velocity, m/s.

#### 3.3.3. Internal energy

The energy associated with molecular motion. The temperature  $T$  of a material is a measure of its internal energy  $U$ :

$$U = f(T) \quad (3.3)$$

#### 3.3.4. Work

Work is done when a force acts through a distance:

$$W = \int_0^l F dx \quad (3.4)$$

where  $F$  = force, N,

$x$  and  $l$  = distance, m.

Work done on a system by its surroundings is conventionally taken as negative; work done by the system on the surroundings as positive.

Where the work arises from a change in pressure or volume:

$$W = \int_1^2 P dv \quad (3.5)$$

where  $P$  = pressure, Pa (N/m<sup>2</sup>),

$v$  = volume per unit mass, m<sup>3</sup>/kg.

To integrate this function the relationship between pressure and volume must be known. In process design an estimate of the work done in compressing or expanding a gas is

often required. A rough estimate can be made by assuming either reversible adiabatic (isentropic) or isothermal expansion, depending on the nature of the process.

For isothermal expansion (expansion at constant temperature):

$$Pv = \text{constant}$$

For reversible adiabatic expansion (no heat exchange with the surroundings):

$$Pv^\gamma = \text{constant}$$

where  $\gamma =$  ratio of the specific heats,  $C_p/C_v$ .

The compression and expansion of gases is covered more fully in Section 3.13.

### 3.3.5. Heat

Energy is transferred either as heat or work. A system does not contain “heat”, but the transfer of heat or work to a system changes its internal energy.

Heat taken in by a system from its surroundings is conventionally taken as positive and that given out as negative.

### 3.3.6. Electrical energy

Electrical, and the mechanical forms of energy, are included in the work term in an energy balance. Electrical energy will only be significant in energy balances on electrochemical processes.

## 3.4. THE ENERGY BALANCE

Consider a steady-state process represented by Figure 3.1. The conservation equation can be written to include the various forms of energy.

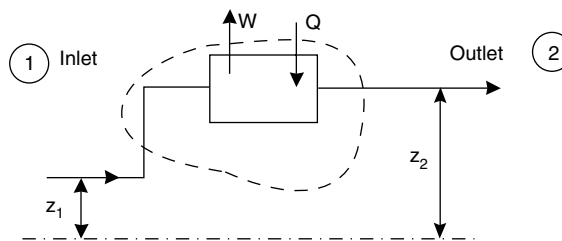


Figure 3.1. General steady-state process

For unit mass of material:

$$U_1 + P_1v_1 + u_1^2/2 + z_1g + Q = U_2 + P_2v_2 + u_2^2/2 + z_2g + W \quad (3.6)$$

The suffixes 1 and 2 represent the inlet and outlet points respectively.  $Q$  is the heat transferred across the system boundary; positive for heat entering the system, negative

for heat leaving the system.  $W$  is the work done by the system; positive for work going from the system to the surroundings, and negative for work entering the system from the surroundings.

Equation 3.6 is a general equation for steady-state systems with flow.

In chemical processes, the kinetic and potential energy terms are usually small compared with the heat and work terms, and can normally be neglected.

It is convenient, and useful, to take the terms  $U$  and  $Pv$  together; defining the term enthalpy, usual symbol  $H$ , as:

$$H = U + Pv$$

Enthalpy is a function of temperature and pressure. Values for the more common substances have been determined experimentally and are given in the various handbooks (see Chapter 8).

Enthalpy can be calculated from specific and latent heat data; see Section 3.5.

If the kinetic and potential energy terms are neglected equation 3.6 simplifies to:

$$H_2 - H_1 = Q - W \quad (3.7)$$

This simplified equation is usually sufficient for estimating the heating and cooling requirements of the various unit operations involved in chemical processes.

As the flow-dependent terms have been dropped, the simplified equation is applicable to both static (non-flow) systems and flow systems. It can be used to estimate the energy requirement for batch processes.

For many processes the work term will be zero, or negligibly small, and equation 3.7 reduces to the simple heat balance equation:

$$Q = H_2 - H_1 \quad (3.8)$$

Where heat is generated in the system; for example, in a chemical reactor:

$$Q = Q_p + Q_s \quad (3.9)$$

$Q_s$  = heat generated in the system. If heat is evolved (exothermic processes)  $Q_s$  is taken as *positive*, and if heat is absorbed (endothermic processes) it is taken as *negative*.

$Q_p$  = process heat added to the system to maintain required system temperature.

Hence:

$$Q_p = H_2 - H_1 - Q_s \quad (3.10)$$

$H_1$  = enthalpy of the inlet stream,

$H_2$  = enthalpy of the outlet stream.

### Example 3.1

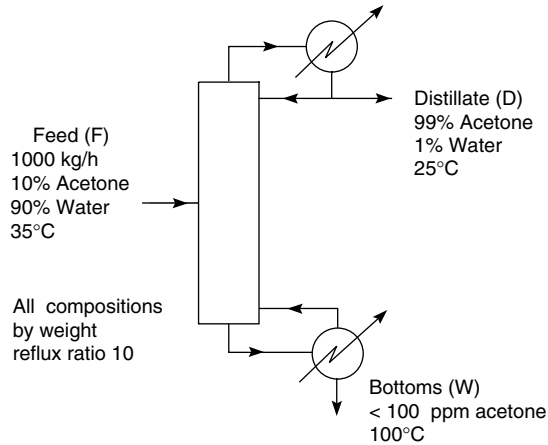
Balance with no chemical reaction. Estimate the steam and the cooling water required for the distillation column shown in the figure.

Steam is available at 25 psig (274 kN/m<sup>2</sup> abs), dry saturated.

The rise in cooling water temperature is limited to 30°C.

Column operates at 1 bar.





## Solution

### Material balance

It is necessary to make a material balance to determine the top and bottoms product flow rates.

Balance on acetone, acetone loss in bottoms neglected.

$$1000 \times 0.1 = D \times 0.99$$

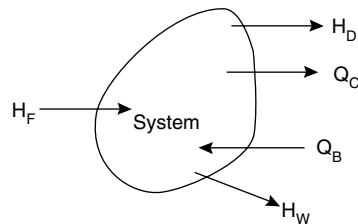
$$\text{Distillate, } D = 101 \text{ kg/h}$$

$$\text{Bottoms, } W = 1000 - 101 = 899 \text{ kg/h}$$

### Energy balance

The kinetic and potential energy of the process streams will be small and can be neglected.

Take the first system boundary to include the reboiler and condenser.



Inputs: reboiler heat input  $Q_B$  + feed sensible heat  $H_F$ .

Outputs: condenser cooling  $Q_C$  + top and bottom product sensible heats  $H_D + H_W$ .

The heat losses from the system will be small if the column and exchangers are properly lagged (typically less than 5 per cent) and will be neglected.

Basis 25°C, 1h.

Heat capacity data, from Volume 1, average values.

Acetone: 25°C to 35°C 2.2 kJ/kg K

Water: 25°C to 100°C 4.2 kJ/kg K

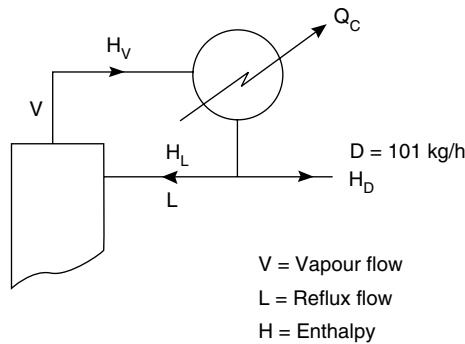
Heat capacities can be taken as additive.

Feed, 10 per cent acetone =  $0.1 \times 2.2 + 0.9 \times 4.2 = 4.00$  kJ/kg K

Tops, 99 per cent acetone, taken as acetone, 2.2 kJ/kg K

Bottoms, as water, 4.2 kJ/kg K.

$Q_C$  must be determined by taking a balance round the condenser.



Reflux ratio (see Chapter 11)

$$R = \frac{L}{D} = 10$$

$$L = 10 \times 101 = 1010 \text{ kg/h}$$

$$V = L + D = 1111 \text{ kg/h}$$

From vapour–liquid equilibrium data:

boiling point of 99 per cent acetone/water = 56.5°C

At steady state:

input = output

$$H_V = H_D + H_L + Q_C,$$

Hence

$$Q_C = H_V - H_D - H_L$$

Assume complete condensation.

Enthalpy of vapour  $H_V = \text{latent} + \text{sensible heat}$ .

There are two ways of calculating the specific enthalpy of the vapour at its boiling point.

- (1) Latent heat of vaporisation at the base temperature + sensible heat to heat the vapour to the boiling point.
- (2) Latent heat of vaporisation at the boiling point + sensible heat to raise liquid to the boiling point.

Values of the latent heat of acetone and water as functions of temperature are given in Volume 1, so the second method will be used.

$$\text{Latent heat acetone at } 56.5^\circ\text{C (330 K)} = 620 \text{ kJ/kg}$$

$$\text{Water at } 56.5^\circ\text{C (330 K)} = 2500 \text{ kJ/kg}$$

Taking latent heats as additive:

$$\begin{aligned} H_V &= 1111[(0.01 \times 2500 + 0.99 \times 620) + (56.5 - 25)2.2] \\ &= 786,699 \text{ kJ/h} \end{aligned}$$

The enthalpy of the top product and reflux are zero, as they are both at the base temperature. Both are liquid, and the reflux will be at the same temperature as the product.

Hence 
$$Q_C = H_V = \underline{\underline{786,699 \text{ kJ/h}}} \quad (218.5 \text{ kW})$$

$Q_B$  is determined from a balance over complete system

Input	Output
$Q_B + H_F$	$Q_C + H_D + H_W$
$H_F = 1000 \times 4.00(35 - 25) = 40,000 \text{ kJ/h}$	
$H_W = 899 \times 4.2(100 - 25) = 283,185 \text{ kJ/h}$	

(boiling point of bottom product taken as  $100^\circ\text{C}$ ).

hence 
$$\begin{aligned} Q_B &= Q_C + H_W + H_D - H_F \\ &= 786,699 + 283,185 + 0 - 40,000 \\ &= \underline{\underline{1,029,884 \text{ kJ/h}}} \quad (286.1 \text{ kW}) \end{aligned}$$

$Q_B$  is supplied by condensing steam.

$$\text{Latent heat of steam (Volume 1)} = 2174 \text{ kJ/kg at } 274 \text{ kN/m}^2$$

$$\text{Steam required} = \frac{1,029,884}{2174} = \underline{\underline{473.7 \text{ kg/h}}}$$

$Q_C$  is removed by cooling water with a temperature rise of  $30^\circ\text{C}$

$$\begin{aligned} Q_C &= \text{water flow} \times 30 \times 4.2 \\ \text{Water flow} &= \frac{786,699}{4.2 \times 30} = \underline{\underline{6244 \text{ kg/h}}} \end{aligned}$$

### 3.5. CALCULATION OF SPECIFIC ENTHALPY

Tabulated values of enthalpy are available only for the more common materials. In the absence of published data the following expressions can be used to estimate the specific enthalpy (enthalpy per unit mass).

For pure materials, with no phase change:

$$H_T = \int_{T_d}^T C_p dT \quad (3.11)$$

where  $H_T$  = specific enthalpy at temperature  $T$ ,

$C_p$  = specific heat capacity of the material, constant pressure,

$T_d$  = the datum temperature.

If a phase transition takes place between the specified and datum temperatures, the latent heat of the phase transition is added to the sensible-heat change calculated by equation 3.11. The sensible-heat calculation is then split into two parts:

$$H_T = \int_{T_d}^{T_p} C_{p1} dT + \int_{T_p}^T C_{p2} dT \quad (3.12)$$

where  $T_p$  = phase transition temperature,

$C_{p1}$  = specific heat capacity first phase, below  $T_p$ ,

$C_{p2}$  = specific heat capacity second phase, above  $T_p$ .

The specific heat at constant pressure will vary with temperature and to use equations 3.11 and 3.12, values of  $C_p$  must be available as a function of temperature. For solids and gases  $C_p$  is usually expressed as an empirical power series equation:

$$C_p = a + bT + cT^2 + dT^3 \quad (3.13a)$$

$$\text{or} \quad C_p = a + bT + cT^{-1/2} \quad (3.13b)$$

Absolute (K) or relative ( $^{\circ}\text{C}$ ) temperature scales may be specified when the relationship is in the form given in equation 3.13a. For equation 3.13b absolute temperatures must be used.

#### Example 3.2

Estimate the specific enthalpy of ethyl alcohol at 1 bar and  $200^{\circ}\text{C}$ , taking the datum temperature as  $0^{\circ}\text{C}$ .

$C_p$  liquid  $0^{\circ}\text{C}$  24.65 cal/mol $^{\circ}\text{C}$

100 $^{\circ}\text{C}$  37.96 cal/mol $^{\circ}\text{C}$

$C_p$  gas ( $t^{\circ}\text{C}$ )  $14.66 + 3.758 \times 10^{-2}t - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3$  cal/mol

Boiling point of ethyl alcohol at 1 bar =  $78.4^{\circ}\text{C}$ .

Latent heat of vaporisation = 9.22 kcal/mol.

**Solution**

*Note:* as the data taken from the literature are given in cal/mol the calculation is carried out in these units and the result converted to SI units.

As no data are given on the exact variation of the  $C_p$  of the liquid with temperature, use an equation of the form  $C_p = a + bt$ , calculating  $a$  and  $b$  from the data given; this will be accurate enough over the range of temperature needed.

$$a = \text{value of } C_p \text{ at } 0^\circ\text{C}, \quad b = \frac{37.96 - 24.65}{100} = 0.133$$

$$\begin{aligned} H_{200^\circ\text{C}} &= \int_0^{78.4} (24.65 + 0.133t) dt + 9.22 \times 10^3 + \int_{78.4}^{200} (14.66 + 3.758 \times 10^{-2}t \\ &\quad - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3) dt \\ &= \left[ 24.65t + 0.133t^2/2 \right]_0^{78.4} + 9.22 \times 10^3 + \left[ 14.66t + 3.758 \times 10^{-2}t^2/2 - 2.091 \right. \\ &\quad \left. \times 10^{-5}t^3/3 + 4.740 \times 10^{-9}t^4/4 \right]_{78.4}^{200} \\ &= 13.95 \times 10^3 \text{ cal/mol} \\ &= 13.95 \times 10^3 \times 4.18 = \underline{\underline{58.31 \times 10^3 \text{ J/mol}}} \end{aligned}$$

Specific enthalpy = 58.31 kJ/mol.

Molecular weight of ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH} = 46$

Specific enthalpy =  $58.31 \times 10^3/46 = \underline{\underline{1268 \text{ kJ/kg}}}$

**3.6. MEAN HEAT CAPACITIES**

The use of mean heat capacities often facilitates the calculation of sensible-heat changes; mean heat capacity over the temperature range  $t_1$  to  $t_2$  is defined by the following equation:

$$C_{pm} = \int_{t_1}^{t_2} C_p dt \div \int_{t_1}^{t_2} dt \quad (3.14)$$

Mean specific heat values are tabulated in various handbooks. If the values are for unit mass, calculated from some standard reference temperature,  $t_r$ , then the change in enthalpy between temperatures  $t_1$  and  $t_2$  is given by:

$$\Delta H = C_{pm,t_2}(t_2 - t_r) - C_{pm,t_1}(t_1 - t_r) \quad (3.15)$$

where  $t_r$  is the reference temperature from which the values of  $C_{pm}$  were calculated.

If  $C_p$  is expressed as a polynomial of the form:  $C_p = a + bt + ct^2 + dt^3$ , then the integrated form of equation 3.14 will be:

$$C_{pm} = \frac{a(t - t_r) + \frac{b}{2}(t^2 - t_r^2) + \frac{c}{3}(t^3 - t_r^3) + \frac{d}{4}(t^4 - t_r^4)}{t - t_r} \quad (3.16)$$

where  $t$  is the temperature at which  $C_{pm}$  is required.

If the reference temperature is taken at 0°C, equation 3.16 reduces to:

$$C_{pm} = a + \frac{bt}{2} + \frac{ct^2}{3} + \frac{dt^3}{4} \quad (3.17)$$

and the enthalpy change from  $t_1$  to  $t_2$  becomes

$$\Delta H = C_{pm,t_2} t_2 - C_{pm,t_1} t_1 \quad (3.18)$$

The use of mean heat capacities is illustrated in Example 3.3.

### Example 3.3

The gas leaving a combustion chamber has the following composition: CO<sub>2</sub> 7.8, CO 0.6, O<sub>2</sub> 3.4, H<sub>2</sub>O 15.6, N<sub>2</sub> 72.6, all volume percentage. Calculate the heat removed if the gas is cooled from 800 to 200°C.

### Solution

Mean heat capacities for the combustion gases are readily available in handbooks and texts on heat and material balances. The following values are taken from K. A. Kobe, *Thermochemistry of Petrochemicals*, reprint No. 44, Pet. Ref. 1958; converted to SI units, J/mol°C, reference temperature 0°C.

°C	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO	H <sub>2</sub> O
200	29.24	29.95	40.15	29.52	34.12
800	30.77	32.52	47.94	31.10	37.38

Heat extracted from the gas in cooling from 800 to 200°C, for each component:

$$= M_c (C_{pm,800} \times 800 - C_{pm,200} \times 200)$$

where  $M_c$  = mols of that component.

Basis 100 mol gas (as analysis is by volume), substitution gives:

$$\begin{aligned} \text{CO}_2 & 7.8(47.94 \times 800 - 40.15 \times 200) = 236.51 \times 10^3 \\ \text{CO} & 0.6(31.10 \times 800 - 29.52 \times 200) = 11.39 \times 10^3 \\ \text{O}_2 & 3.4(32.52 \times 800 - 29.95 \times 200) = 68.09 \times 10^3 \\ \text{H}_2\text{O} & 15.6(37.38 \times 800 - 34.12 \times 200) = 360.05 \times 10^3 \\ \text{N}_2 & 72.6(30.77 \times 800 - 29.24 \times 200) = \underline{1362.56 \times 10^3} \\ & = \underline{\underline{2038.60 \text{ kJ/100 mol}}} \\ & = \underline{\underline{20.39 \text{ kJ/mol}}} \end{aligned}$$

### 3.7. THE EFFECT OF PRESSURE ON HEAT CAPACITY

The data on heat capacities given in the handbooks, and in Appendix A, are, usually for the ideal gas state. Equation 3.13a should be written as:

$$C_p^\circ = a + bT + cT^2 + dT^3 \quad (3.19)$$

where the superscript  $^\circ$  refers to the ideal gas state.

The ideal gas values can be used for the real gases at low pressures. At high pressures the effect of pressure on the specific heat may be appreciable.

Edmister (1948) published a generalised plot showing the isothermal pressure correction for real gases as a function of the reduced pressure and temperature. His chart, converted

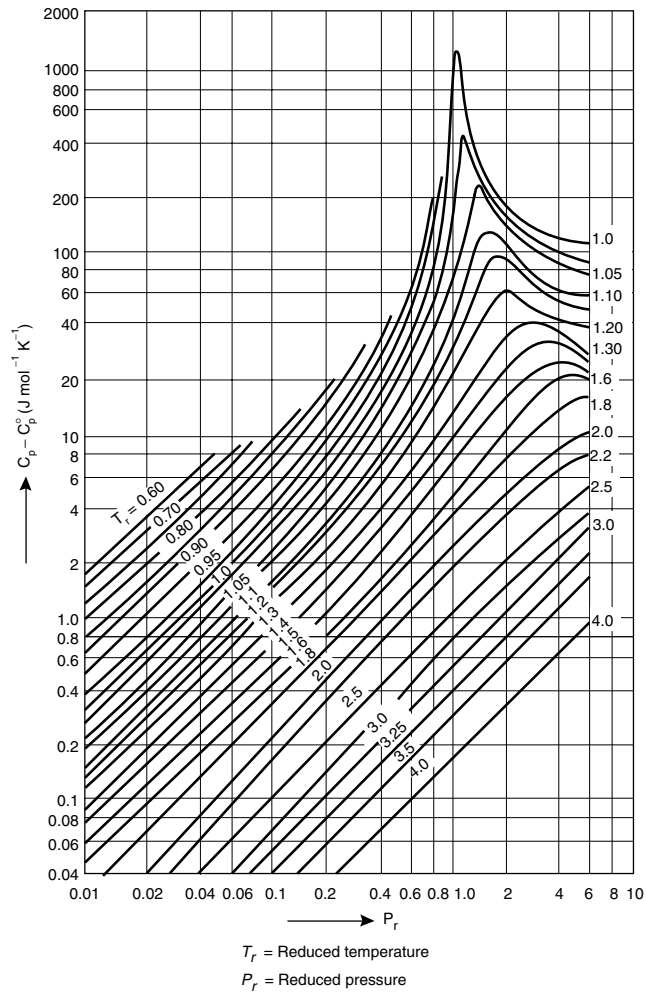


Figure 3.2. Excess heat capacity chart (reproduced from Sterbacek *et al.* (1979), with permission)

to SI units, is shown as Figure 3.2. Edmister's chart was based on hydrocarbons, but can be used for other materials to give an indication of the likely error if the ideal gas specific heat values are used without corrections.

The method is illustrated in Example 3.4.

### Example 3.4

The ideal state heat capacity of ethylene is given by the equation:

$$C_p^\circ = 3.95 + 15.6 \times 10^{-2}T - 8.3 \times 10^{-5}T^2 + 17.6 \times 10^{-9}T^3 \text{ J/mol K}$$

Estimate the value at 10 bar and 300 K.

### Solution

Ethylene: critical pressure 50.5 bar  
critical temperature 283 K

$$\begin{aligned} C_p^\circ &= 3.95 + 15.6 \times 10^{-2} \times 300 - 8.3 \times 10^{-5} \times 300^2 + 17.6 \times 10^{-9} \times 300^3 \\ &= \underline{\underline{43.76 \text{ J/mol K}}} \end{aligned}$$

$$P_r = \frac{10}{50.5} = \underline{\underline{0.20}}$$

$$T_r = \frac{300}{283} = \underline{\underline{1.06}}$$

From Figure 3.2:

$$C_p - C_p^\circ \simeq \underline{\underline{5 \text{ J/mol K}}}$$

So 
$$C_p = 43.76 + 5 = \underline{\underline{\approx 49 \text{ J/mol K}}}$$

The error in  $C_p$  if the ideal gas value were used uncorrected would be approximately 10 per cent.

## 3.8. ENTHALPY OF MIXTURES

For gases, the heats of mixing are usually negligible and the heat capacities and enthalpies can be taken as additive without introducing any significant error into design calculations; as was done in Example 3.3.

$$C_p(\text{mixture}) = x_a C_{p_a} + x_b C_{p_b} + x_c C_{p_c} + \dots \quad (3.20)$$

where  $x_a$ ,  $x_b$ ,  $x_c$ , etc., are the mol fractions of the components  $a$ ,  $b$ ,  $c$ .

For mixtures of liquids and for solutions, the heat of mixing (heat of solution) may be significant, and so must be included when calculating the enthalpy of the mixture.

For binary mixtures, the specific enthalpy of the mixture at temperature  $t$  is given by:

$$H_{\text{mixture},t} = x_a H_{a,t} + x_b H_{b,t} + \Delta H_{m,t} \quad (3.21)$$

where  $H_{a,t}$  and  $H_{b,t}$  are the specific enthalpies of the components  $a$  and  $b$  and  $-\Delta H_{m,t}$  is the heat of mixing when 1 mol of solution is formed, at temperature  $t$ .



Heats of mixing and heats of solution are determined experimentally and are available in the handbooks for the more commonly used solutions.

If no values are available, judgement must be used to decide if the heat of mixing for the system is likely to be significant.

For organic solutions the heat of mixing is usually small compared with the other heat quantities, and can usually be neglected when carrying out a heat balance to determine the process heating or cooling requirements.

The heats of solution of organic and inorganic compounds in water can be large, particularly for the strong mineral acids and alkalies.

### 3.8.1. Integral heats of solution

Heats of solution are dependent on concentration. The integral heat of solution at any given concentration is the cumulative heat released, or absorbed, in preparing the solution from pure solvent and solute. The integral heat of solution at infinite dilution is called the *standard integral heat of solution*.

Tables of the integral heat of solution over a range of concentration, and plots of the integral heat of solution as a function of concentration, are given in the handbooks for many of the materials for which the heat of solution is likely to be significant in process design calculations.

The integral heat of solution can be used to calculate the heating or cooling required in the preparation of solutions, as illustrated in Example 3.5.

#### Example 3.5

A solution of NaOH in water is prepared by diluting a concentrated solution in an agitated, jacketed, vessel. The strength of the concentrated solution is 50 per cent w/w and 2500 kg of 5 per cent w/w solution is required per batch. Calculate the heat removed by the cooling water if the solution is to be discharged at a temperature of 25°C. The temperature of the solutions fed to the vessel can be taken to be 25°C.

#### Solution

Integral heat of solution of NaOH – H<sub>2</sub>O, at 25°C

mols H <sub>2</sub> O/mol NaOH	$-\Delta H_{\text{soln}}^{\circ}$ kJ/mol NaOH
2	22.9
4	34.4
5	37.7
10	42.5
infinite	42.9

Conversion of weight per cent to mol/mol:

$$50 \text{ per cent w/w} = 50/18 \div 50/40 = 2.22 \text{ mol H}_2\text{O/mol NaOH}$$

$$5 \text{ per cent w/w} = 95/18 \div 5/40 = 42.2 \text{ mol H}_2\text{O/mol NaOH}$$

From a plot of the integral heats of solution versus concentration,

$$\begin{aligned} -\Delta H_{\text{soln}}^{\circ} \text{ 2.22 mol/mol} &= 27.0 \text{ kJ/mol NaOH} \\ &42.2 \text{ mol/mol} = 42.9 \text{ kJ/mol NaOH} \end{aligned}$$

Heat liberated in the dilution per mol NaOH

$$= 42.9 - 27.0 = \underline{\underline{15.9 \text{ kJ}}}$$

Heat released per batch = mol NaOH per batch  $\times$  15.9

$$= \frac{2500 \times 10^3 \times 0.05}{40} \times 15.9 = \underline{\underline{49.7 \times 10^3 \text{ kJ}}}$$

Heat transferred to cooling water, neglecting heat losses,

$$\underline{\underline{49.7 \text{ MJ per batch}}}$$

In Example 3.5 the temperature of the feeds and final solution have been taken as the same as the standard temperature for the heat of solution, 25°C, to simplify the calculation. Heats of solution are analogous to heats of reaction, and examples of heat balances on processes where the temperatures are different from the standard temperature are given in the discussion of heats of reaction, Section 3.10.

### 3.9. ENTHALPY-CONCENTRATION DIAGRAMS

The variation of enthalpy for binary mixtures is conveniently represented on a diagram. An example is shown in Figure 3.3. The diagram shows the enthalpy of mixtures of ammonia and water versus concentration; with pressure and temperature as parameters. It covers the phase changes from solid to liquid to vapour, and the enthalpy values given include the latent heats for the phase transitions.

The enthalpy is per kg of the mixture (ammonia + water)

Reference states: enthalpy ammonia at  $-77^{\circ}\text{C}$  = zero

enthalpy water at  $0^{\circ}\text{C}$  = zero

Enthalpy-concentration diagrams greatly facilitate the calculation of energy balances involving concentration and phase changes; this is illustrated in Example 3.6.

#### Example 3.6

Calculate the maximum temperature when liquid ammonia at  $40^{\circ}\text{C}$  is dissolved in water at  $20^{\circ}\text{C}$  to form a 10 per cent solution.

#### Solution

The maximum temperature will occur if there are no heat losses (adiabatic process). As no heat or material is removed, the problem can be solved graphically in the enthalpy-concentration diagram (Figure 3.3). The mixing operation is represented on the diagram

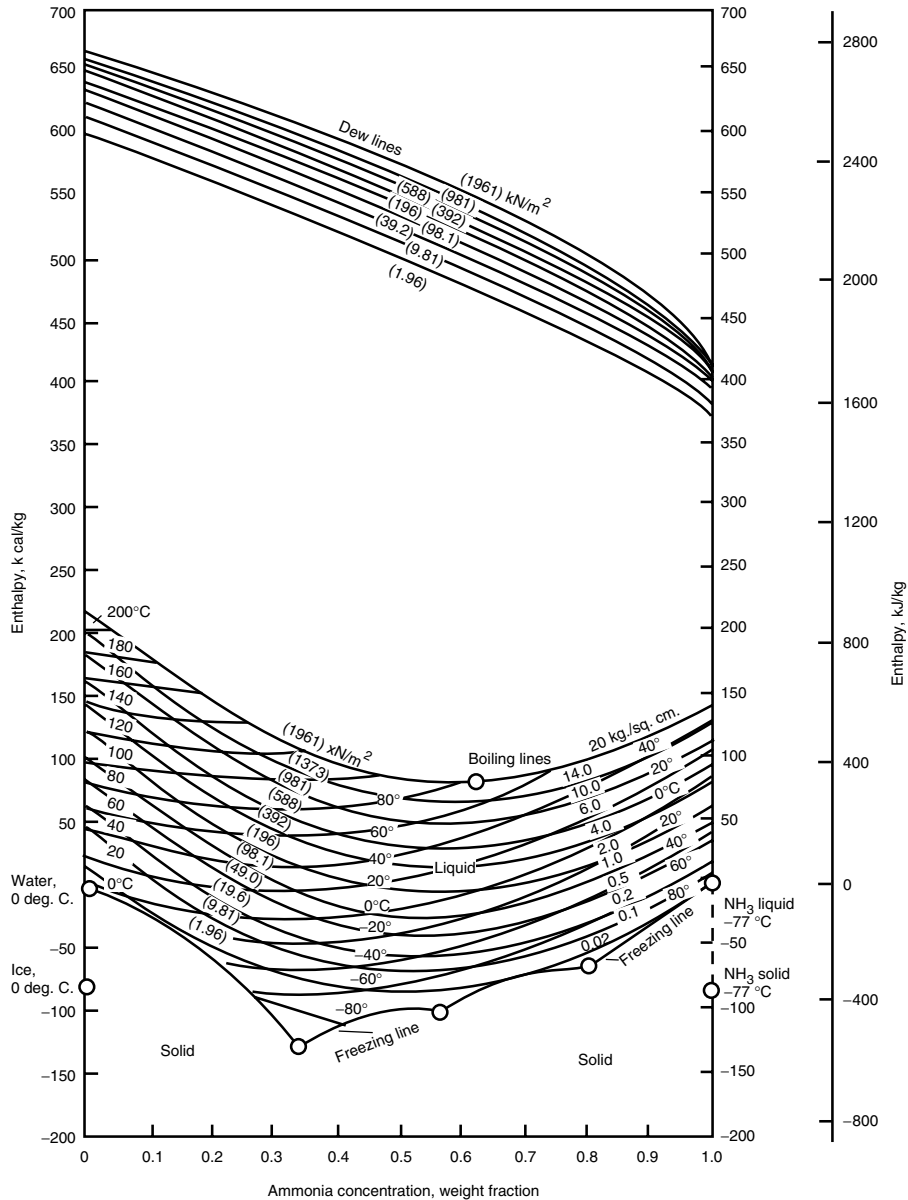
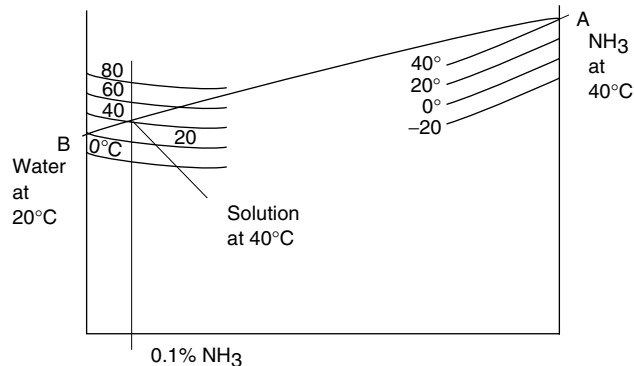


Figure 3.3. Enthalpy-concentration diagram for aqueous ammonia. Reference states: enthalpies of liquid water at  $0^{\circ}\text{C}$  and liquid ammonia at  $-77^{\circ}\text{C}$  are zero. (Bosniakovic, *Technische Thermodynamik*, T. Steinkopff, Leipzig, 1935)

by joining the point A representing pure ammonia at  $40^{\circ}\text{C}$  with the point B representing pure water at  $20^{\circ}\text{C}$ . The value of the enthalpy of the mixture lies on a vertical line at the required concentration, 0.1. The temperature of the mixture is given by the intersection of this vertical line with the line AB. This method is an application of the “lever rule” for phase diagrams. For a more detailed explanation of the method and further examples see

Himmelbau (1995) or any of the general texts on material and energy balances listed at the end of Chapter 2. The Ponchon-Savarit graphical method used in the design of distillation columns, described in Volume 2, Chapter 11, is a further example of the application of the lever rule, and the use of enthalpy-concentration diagrams.



### 3.10. HEATS OF REACTION

If a process involves chemical reaction, heat will normally have to be added or removed. The amount of heat given out in a chemical reaction depends on the conditions under which the reaction is carried out. The standard heat of reaction is the heat released when the reaction is carried out under standard conditions: pure components, pressure 1 atm (1.01325 bar), temperature usually, but not necessarily, 25°C.

Values for the standard heats of reactions are given in the literature, or may be calculated by the methods given in Sections 3.11 and 3.12.

When quoting heats of reaction the basis should be clearly stated. Either by giving the chemical equation, for example:



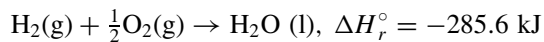
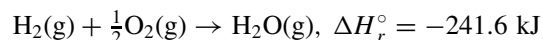
(The equation implies that the quantity of reactants and products are mols)

Or, by stating to which quantity the quoted value applies:

$$\Delta H_r^\circ = -56.68 \text{ kJ per mol NO}_2$$

The reaction is exothermic and the enthalpy change  $\Delta H_r^\circ$  is therefore *negative*. The heat of reaction  $-\Delta H_r^\circ$  is *positive*. The superscript  $^\circ$  denotes a value at *standard* conditions and the subscript *r* implies that a chemical reaction is involved.

The state of the reactants and products (gas, liquid or solid) should also be given, if the reaction conditions are such that they may exist in more than one state; for example:



The difference between the two heats of reaction is the latent heat of the water formed.

In process design calculations it is usually more convenient to express the heat of reaction in terms of the mols of product produced, for the conditions under which the reaction is carried out, kJ/mol product.

Standard heats of reaction can be converted to other reaction temperatures by making a heat balance over a hypothetical process, in which the reactants are brought to the standard temperature, the reaction carried out, and the products then brought to the required reaction temperature; as illustrated in Figure 3.4.

$$\Delta H_{r,t} = \Delta H_r^\circ + \Delta H_{\text{prod.}} - \Delta H_{\text{react.}} \quad (3.22)$$

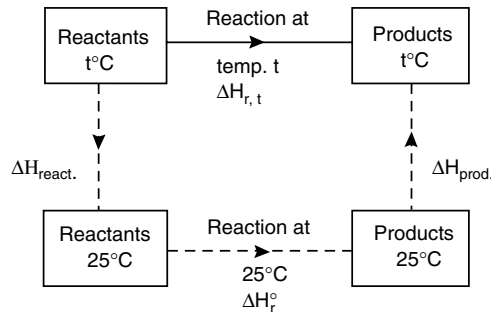


Figure 3.4.  $\Delta H_r$  at temperature  $t$

where  $-\Delta H_{r,t}$  = heat of reaction at temperature  $t$ ,

$\Delta H_{\text{react.}}$  = enthalpy change to bring reactants to standard temperature,

$\Delta H_{\text{prod.}}$  = enthalpy change to bring products to reaction temperature,  $t$ .

For practical reactors, where the reactants and products may well be at temperatures different from the reaction temperature, it is best to carry out the heat balance over the actual reactor using the standard temperature ( $25^\circ\text{C}$ ) as the datum temperature; the standard heat of reaction can then be used without correction.

It must be emphasised that it is unnecessary to correct a heat of reaction to the reaction temperature for use in a reactor heat-balance calculation. To do so is to carry out two heat balances, whereas with a suitable choice of datum only one need be made. For a practical reactor, the heat added (or removed)  $Q_p$  to maintain the design reactor temperature will be given by (from equation 3.10):

$$Q_p = H_{\text{products}} - H_{\text{reactants}} - Q_r \quad (3.23)$$

where  $H_{\text{products}}$  is the *total* enthalpy of the product streams, including unreacted materials and by-products, evaluated from a datum temperature of  $25^\circ\text{C}$ ;

$H_{\text{reactants}}$  is the total enthalpy of the feed streams, including excess reagent and inerts, evaluated from a datum of  $25^\circ\text{C}$ ;

$Q_r$  is the total heat generated by the reactions taking place, evaluated from the standard heats of reaction at 25°C (298 K).

$$Q_r = \sum -\Delta H_r^\circ \times (\text{mol of product formed}) \quad (3.24)$$

where  $-\Delta H_r^\circ$  is the standard heat of reaction per mol of the particular product.

*Note:* A negative sign is necessary in equation 3.24 as  $Q_r$  is positive when heat is evolved by the reaction, whereas the standard enthalpy change will be negative for exothermic reactions.  $Q_p$  will be negative when cooling is required (see Section 3.4).

### 3.10.1. Effect of pressure on heats of reaction

Equation 3.22 can be written in a more general form:

$$\begin{aligned} \Delta H_{r,P,T} = \Delta H_r^\circ + \int_1^P \left[ \left( \frac{\partial H_{\text{prod.}}}{\partial P} \right)_T - \left( \frac{\partial H_{\text{react.}}}{\partial P} \right)_T \right] dP \\ + \int_{298}^T \left[ \left( \frac{\partial H_{\text{prod.}}}{\partial T} \right)_P - \left( \frac{\partial H_{\text{react.}}}{\partial T} \right)_P \right] dT \end{aligned} \quad (3.25)$$

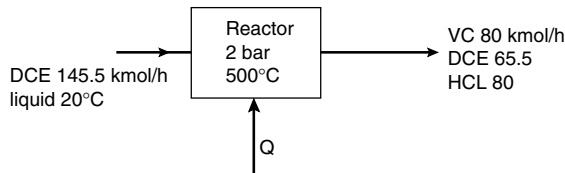
If the effect of pressure is likely to be significant, the change in enthalpy of the products and reactants, from the standard conditions, can be evaluated to include both the effects of temperature and pressure (for example, by using tabulated values of enthalpy) and the correction made in a similar way to that for temperature only.

### Example 3.7

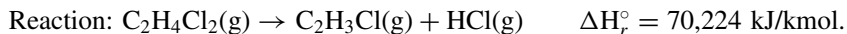
Illustrates the manual calculation of a reactor heat balance.

Vinyl chloride (VC) is manufactured by the pyrolysis of 1,2-dichloroethane (DCE). The reaction is endothermic. The flow-rates to produce 5000 kg/h at 55 per cent conversion are shown in the diagram (see Example 2.13).

The reactor is a pipe reactor heated with fuel gas, gross calorific value 33.5 MJ/m<sup>3</sup>. Estimate the quantity of fuel gas required.



### Solution



The small quantity of impurities, less than 1 per cent, that would be present in the feed have been neglected for the purposes of this example. Also, the yield of VC has been taken as 100 per cent. It would be in the region of 99 per cent at 55 per cent conversion.

Heat capacity data, for vapour phase

$$C_p^\circ = a + bT + cT^2 + dT^3 \quad \text{kJ/kmolK}$$

	$a$	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
VC	5.94	20.16	-15.34	47.65
HCl	30.28	-0.761	1.325	-4.305
DCE	20.45	23.07	-14.36	33.83

for liquid phase: DCE at 20°C,  $C_p = 116$  kJ/kmol K,

taken as constant over temperature rise from 20 to 25°C.

Latent heat of vaporisation of DCE at 25°C = 34.3 MJ/kmol.

At 2 bar pressure the change in  $C_p$  with pressure will be small and will be neglected. Take base temperature as 25°C (298 K), the standard state for  $\Delta H_r^\circ$ .

$$\text{Enthalpy of feed} = 145.5 \times 116(293 - 298) = -84,390 \text{ kJ/h} = \underline{\underline{-84.4 \text{ MJ/h}}}$$

$$\text{Enthalpy of product stream} = \int_{298}^{773} \sum (n_i C_p) dT$$

Component	$n_i$ (mol/h)	$n_i a$	$n_i b \times 10^2$	$n_i c \times 10^5$	$n_i d \times 10^9$
VC	80	475.2	1612.8	-1227.2	3812.0
HCl	80	2422.4	-60.88	106.0	-344.4
DCE	65.5	1339.5	1511.0	-940.6	2215.9
$\sum n_i C_p$		4237.1	3063.0	-2061.8	5683.5

$$\begin{aligned} & \int_{298}^{773} \sum n_i C_p dT \\ &= \int_{298}^{773} (4237.1 + 3063.0 \times 10^{-2}T - 2061.8 \times 10^{-5}T^2 + 5683.5 \times 10^{-9}T^3) dT \\ &= \underline{\underline{7307.3 \text{ MJ/h}}} \end{aligned}$$

Heat consumed in system by the endothermic reaction =  $\Delta H_r^\circ \times$  mols produced

$$= 70,224 \times 80 = 5,617,920 \text{ kJ/h} = \underline{\underline{5617.9 \text{ MJ/h}}}$$

Heat to vaporise feed (gas phase reaction)

$$= 34.3 \times 145.5 = \underline{\underline{4990.7 \text{ MJ/h}}}$$

Heat balance:

$$\text{Output} = \text{Input} + \text{consumed} + Q$$

$$Q = H_{\text{product}} - H_{\text{feed}} + \text{consumed}$$

$$= 7307.3 - (-84.4) + (5617.9 + 4990.7) = \underline{\underline{18,002.3 \text{ MJ/h}}}$$

Taking the overall efficiency of the furnace as 70% the gas rate required

$$\begin{aligned}
 &= \frac{\text{Heat input}}{(\text{calorific value} \times \text{efficiency})} \\
 &= \frac{18,002.3}{33.5 \times 0.7} = \underline{\underline{768 \text{ m}^3/\text{h}}}
 \end{aligned}$$

### 3.11. STANDARD HEATS OF FORMATION

The standard enthalpy of formation  $\Delta H_f^\circ$  of a compound is defined as the enthalpy change when one mol of the compound is formed from its constituent elements in the standard state. The enthalpy of formation of the elements is taken as zero. The standard heat of any reaction can be calculated from the heats of formation  $-\Delta H_f^\circ$  of the products and reactants; if these are available or can be estimated.

Conversely, the heats of formation of a compound can be calculated from the heats of reaction; for use in calculating the standard heat of reaction for other reactions.

The relationship between standard heats of reaction and formation is given by equation 3.26 and illustrated by Examples 3.8 and 3.9

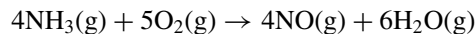
$$\Delta H_r^\circ = \sum \Delta H_f^\circ, \text{ products} - \sum \Delta H_f^\circ, \text{ reactants} \quad (3.26)$$

A comprehensive list of enthalpies of formation is given in Appendix D.

As with heats of reaction, the state of the materials must be specified when quoting heats of formation.

#### Example 3.8

Calculate the standard heat of the following reaction, given the enthalpies of formation:



Standard enthalpies of formation kJ/mol

NH <sub>3</sub> (g)	-46.2
NO(g)	+90.3
H <sub>2</sub> O(g)	-241.6

#### Solution

*Note:* the enthalpy of formation of O<sub>2</sub> is zero.

$$\begin{aligned}
 \Delta H_r^\circ &= \sum \Delta H_f^\circ, \text{ products} - \sum \Delta H_f^\circ, \text{ reactants} \\
 &= (4 \times 90.3 + 6 \times (-241.6)) - (4 \times (-46.2)) \\
 &= \underline{\underline{-903.6 \text{ kJ/mol}}}
 \end{aligned}$$

Heat of reaction  $-\Delta H_r^\circ = \underline{\underline{904 \text{ kJ/mol}}}$



### 3.12. HEATS OF COMBUSTION

The heat of combustion of a compound  $-\Delta H_c^\circ$  is the standard heat of reaction for complete combustion of the compound with oxygen. Heats of combustion are relatively easy to determine experimentally. The heats of other reactions can be easily calculated from the heats of combustion of the reactants and products.

The general expression for the calculation of heats of reaction from heats of combustion is

$$\Delta H_r^\circ = \sum \Delta H_c^\circ, \text{ reactants} - \sum \Delta H_c^\circ, \text{ products} \quad (3.27)$$

*Note:* the product and reactant terms are the opposite way round to that in the expression for the calculation from heats of formation (equation 3.26).

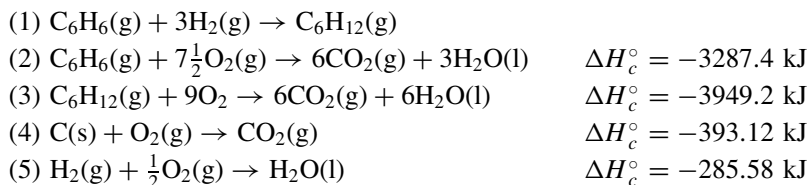
For compounds containing nitrogen, the nitrogen will not be oxidised to any significant extent in combustion and is taken to be unchanged in determining the heat of combustion.

*Caution.* Heats of combustion are large compared with heats of reaction. Do not round off the numbers before subtraction; round off the difference.

Two methods of calculating heats of reaction from heats of combustion are illustrated in Example 3.9.

#### Example 3.9

Calculate the standard heat of reaction for the following reaction: the hydrogenation of benzene to cyclohexane.



*Note:* unlike heats of formation, the standard state of water for heats of combustion is liquid. Standard pressure and temperature are the same 25°C, 1 atm.

#### Solution

##### Method 1

Using the more general equation 3.26

$$\Delta H_r^\circ = \sum \Delta H_f^\circ, \text{ products} - \sum \Delta H_f^\circ, \text{ reactants}$$

the enthalpy of formation of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{H}_{12}$  can be calculated, and from these values the heat of reaction (1).

From reaction (2)

$$\Delta H_c^\circ(\text{C}_6\text{H}_6) = 6 \times \Delta H_c^\circ(\text{CO}_2) + 3 \times \Delta H_c^\circ(\text{H}_2\text{O}) - \Delta H_f^\circ(\text{C}_6\text{H}_6)$$

$$3287.4 = 6(-393.12) + 3(-285.58) - \Delta H_f^\circ(\text{C}_6\text{H}_6)$$

$$\Delta H_f^\circ(\text{C}_6\text{H}_6) = -3287.4 - 3215.52 = \underline{\underline{71.88 \text{ kJ/mol}}}$$

From reaction (3)

$$\Delta H_c^\circ(\text{C}_6\text{H}_{12}) = -3949.2 = 6(-393.12) + 6(-285.58) - \Delta H_f^\circ(\text{C}_6\text{H}_{12})$$

$$\Delta H_f^\circ(\text{C}_6\text{H}_{12}) = 3949.2 - 4072.28 = \underline{\underline{-123.06 \text{ kJ/mol}}}$$

$$\Delta H_r^\circ = \Delta H_f^\circ(\text{C}_6\text{H}_{12}) - \Delta H_f^\circ(\text{C}_6\text{H}_6)$$

$$\Delta H_r^\circ = (-123.06) - (71.88) = \underline{\underline{-195 \text{ kJ/mol}}}$$

*Note:* enthalpy of formation of  $\text{H}_2$  is zero.

### Method 2

Using equation 3.27

$$\begin{aligned} \Delta H_r^\circ &= (\Delta H_c^\circ(\text{C}_6\text{H}_6) + 3 \times \Delta H_c^\circ(\text{H}_2)) - \Delta H_c^\circ(\text{C}_6\text{H}_{12}) \\ &= (-3287.4 + 3(-285.88)) - (-3949.2) = \underline{\underline{-196 \text{ kJ/mol}}} \end{aligned}$$

Heat of reaction  $-\Delta H_r^\circ = \underline{\underline{196 \text{ kJ/mol}}}$

## 3.13. COMPRESSION AND EXPANSION OF GASES

The work term in an energy balance is unlikely to be significant unless a gas is expanded or compressed as part of the process. To compute the pressure work term:

$$-W = \int_1^2 P \, dv \quad (\text{equation 3.5})$$

a relationship between pressure and volume during the expansion is needed.

If the compression or expansion is isothermal (at constant temperature) then for unit mass of an ideal gas:

$$Pv = \text{constant} \quad (3.28)$$

and the work done, 
$$-W = P_1 v_1 \ln \frac{P_2}{P_1} = \frac{RT_1}{M} \ln \frac{P_2}{P_1} \quad (3.29)$$

where  $P_1$  = initial pressure,

$P_2$  = final pressure,

$v_1$  = initial volume.

In industrial compressors or expanders the compression or expansion path will be “polytropic”, approximated by the expression:

$$Pv^n = \text{constant} \quad (3.30)$$

The work produced (or required) is given by the general expression (see Volume 1, Chapter 8):

$$-W = P_1 v_1 \frac{n}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] = Z \frac{\mathbf{R} T_1}{M} \frac{n}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] \quad (3.31)$$

where  $Z$  = compressibility factor (1 for an ideal gas),

$\mathbf{R}$  = universal gas constant,  $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ,

$T_1$  = inlet temperature, K,

$M$  = molecular mass (weight) of gas,

$W$  = work done, J/kg.

The value of  $n$  will depend on the design and operation of the machine.

The energy required to compress a gas, or the energy obtained from expansion, can be estimated by calculating the ideal work and applying a suitable efficiency value. For reciprocating compressors the isentropic work is normally used ( $n = \gamma$ ) (see Figure 3.7); and for centrifugal or axial machines the polytropic work (see Figure 3.6 and Section 3.13.2).

### 3.13.1. Mollier diagrams

If a Mollier diagram (enthalpy-pressure-temperature-entropy) is available for the working fluid the isentropic work can be easily calculated.

$$W = H_1 - H_2 \quad (3.32)$$

where  $H_1$  is the specific enthalpy at the pressure and temperature corresponding to point 1, the initial gas conditions,

$H_2$  is the specific enthalpy corresponding to point 2, the final gas condition.

Point 2 is found from point 1 by tracing a path (line) of constant entropy on the diagram.

The method is illustrated in Example 3.10.

#### Example 3.10

Methane is compressed from 1 bar and 290 K to 10 bar. If the isentropic efficiency is 0.85, calculate the energy required to compress 10,000 kg/h. Estimate the exit gas temperature.

#### Solution

From the Mollier diagram, shown diagrammatically in Figure 3.5

$$H_1 = 4500 \text{ cal/mol},$$

$$H_2 = 6200 \text{ cal/mol (isentropic path)},$$

$$\text{Isentropic work} = 6200 - 4500$$

$$= \underline{\underline{1700 \text{ cal/mol}}}$$

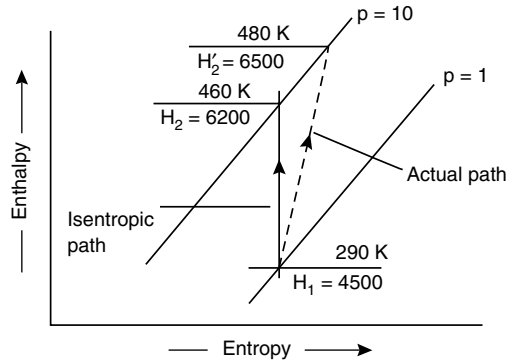


Figure 3.5. Mollier diagram, methane

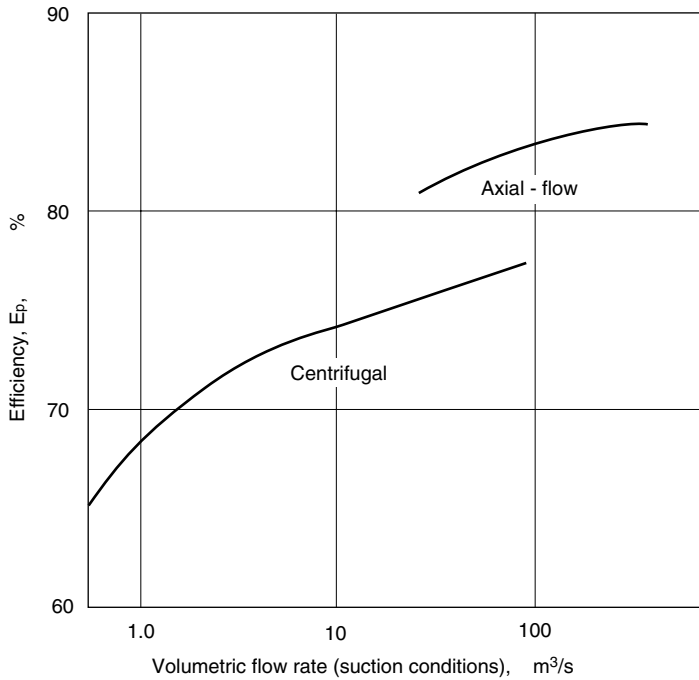


Figure 3.6. Approximate polytropic efficiencies centrifugal and axial-flow compressors

For an isentropic efficiency of 0.85:

$$\text{Actual work done on gas} = \frac{1700}{0.85} = \underline{\underline{2000 \text{ cal/mol}}}$$

So, actual final enthalpy

$$H'_2 = H_1 + 2000 = \underline{\underline{6500 \text{ cal/mol}}}$$

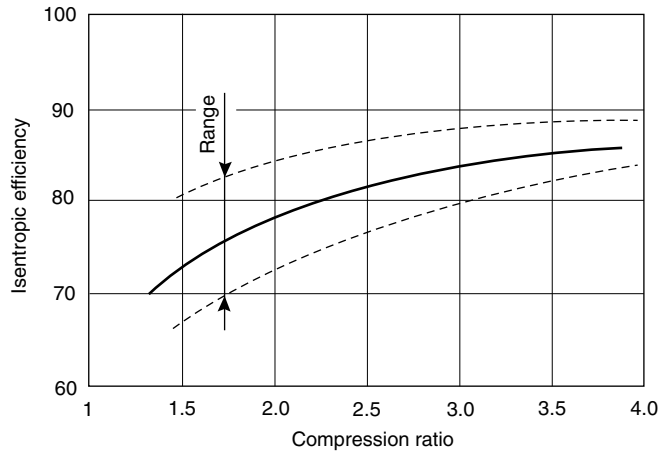


Figure 3.7. Typical efficiencies for reciprocating compressors

From Mollier diagram, if all the extra work is taken as irreversible work done on the gas, the exit gas temperature = 480 K

Molecular weight methane = 16

$$\begin{aligned}
 \text{Energy required} &= (\text{mols per hour}) \times (\text{specific enthalpy change}) \\
 &= \frac{10,000}{16} \times 2000 \times 10^3 \\
 &= 1.25 \times 10^9 \text{ cal/h} \\
 &= 1.25 \times 10^9 \times 4.187 \\
 &= 5.23 \times 10^9 \text{ J/h} \\
 \text{Power} &= \frac{5.23 \times 10^9}{3600} = \underline{\underline{1.45 \text{ MW}}}
 \end{aligned}$$

### 3.13.2. Polytropic compression and expansion

If no Mollier diagram is available, it is more difficult to estimate the ideal work in compression or expansion processes. Schultz (1962) gives a method for the calculation of the polytropic work, based on two generalised compressibility functions,  $X$  and  $Y$ ; which supplement the familiar compressibility factor  $Z$ .

$$X = \frac{T}{V} \left( \frac{\partial V}{\partial T} \right)_P - 1 \quad (3.33)$$

$$Y = -\frac{P}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (3.34)$$

His charts for  $X$  and  $Y$  as functions of reduced temperature and pressure are reproduced as Figures 3.9 and 3.10. The functions are used to determine the polytropic exponent  $n$

for use in equation 3.31; and a polytropic temperature exponent  $m$  for use in the following equation:

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^m \quad (3.35)$$

where

$$m = \frac{ZR}{C_p} \left( \frac{1}{E_p} + X \right) \text{ for compression,} \quad (3.36)$$

$$m = \frac{ZR}{C_p} (E_p + X) \text{ for expansion} \quad (3.37)$$

$E_p$  is the polytropic efficiency, defined by:

$$\text{for compression } E_p = \frac{\text{polytropic work}}{\text{actual work required}}$$

$$\text{for expansion } E_p = \frac{\text{actual work obtained}}{\text{polytropic work}}$$

An estimate of  $E_p$  can be obtained from Figure 3.6.

$$n = \frac{1}{Y - m(1 + X)} \quad (3.38)$$

At conditions well removed from the critical conditions equations 3.36, 3.37 and 3.38 reduce to:

$$m = \frac{(\gamma - 1)}{\gamma E_p} \quad (3.36a)$$

$$m = \frac{(\gamma - 1)E_p}{\gamma} \quad (3.37a)$$

$$n = \frac{1}{1 - m} \quad (3.38a)$$

These expressions can be used to calculate the polytropic work and outlet temperature by substitution in equations 3.31 and 3.35. They can also be used to make a first estimate of  $T_2$  in order to estimate the mean reduced temperature for use with Figures 3.9 and 3.10.

The use of Schultz's method is illustrated in Examples 3.11 and 3.16.

### Example 3.11

Estimate the power required to compress 5000 kmol/h of HCl at 5 bar, 15°C, to 15 bar.

### Solution

For HCl,  $P_c = 82$  bar,  $T_c = 324.6$  K

$$C_p^\circ = 30.30 - 0.72 \times 10^{-2}T + 12.5 \times 10^{-6}T^2 - 3.9 \times 10^{-9}T^3 \text{ kJ/kmol K}$$

Estimate  $T_2$  from equations 3.35 and 3.36a.

For diatomic gases  $\gamma \simeq 1.4$ .

Note:  $\gamma$  could be estimated from the relationship  $\gamma = \frac{C_p}{C_v} = \frac{C_p}{C_p - R}$

At the inlet conditions, the flow rate in  $\text{m}^3/\text{s}$

$$= \frac{5000}{3600} \times 22.4 \times \frac{288}{273} \times \frac{1}{5} = 6.56$$

From Figure 3.6  $E_p = 0.73$

From equations 3.36a and 3.35 
$$m = \frac{1.4 - 1}{1.4 \times 0.73} = 0.39$$

$$T_2 = 288 \left( \frac{15}{5} \right)^{0.39} = 442 \text{ K}$$

$$T_r (\text{mean}) = \frac{442 + 228}{2 \times 324.6} = 1.03$$

$$P_r (\text{mean}) = \frac{5 + 15}{2 \times 82} = 0.12$$

At  $T_{(\text{mean})} C_p^\circ = 29.14 \text{ kJ/kmol K}$

Correction for pressure from Figure 3.2, 2 kJ/kmol K

$$C_p = 29.14 + 2 \simeq 31 \text{ kJ/kmol K}$$

From Figures 3.8, 3.9 and 3.10 at mean conditions:

$$X = 0.18, \quad Y = 1.04, \quad Z = 0.97$$

$$Z \text{ at inlet conditions} = 0.98$$

From equations 3.36 and 3.38

$$m = \frac{0.97 \times 8.314}{31} \left( \frac{1}{0.73} + 0.18 \right) = \underline{\underline{0.40}}$$

$$n = \frac{1}{1.04 - 0.4(1 + 0.18)} = \underline{\underline{1.76}}$$

From equation 3.31

$$W \text{ polytropic} = 0.98 \times 288 \times 8.314 \times \frac{1.76}{1.76 - 1} \left( \left( \frac{15}{5} \right)^{(1.76-1)/1.76} - 1 \right)$$

$$= \underline{\underline{3299 \text{ kJ/kmol}}}$$

$$\text{Actual work required} = \frac{\text{polytropic work}}{E_p}$$

$$= \frac{3299}{0.73} = \underline{\underline{4520 \text{ kJ/kmol}}}$$

$$\text{Power} = \frac{4520}{3600} \times 5000 = 6275 \text{ kW}$$

Say, 6.3 MW

$$T_2 = 288 \left( \frac{15}{5} \right)^{0.4} = \underline{\underline{447 \text{ K}}}$$

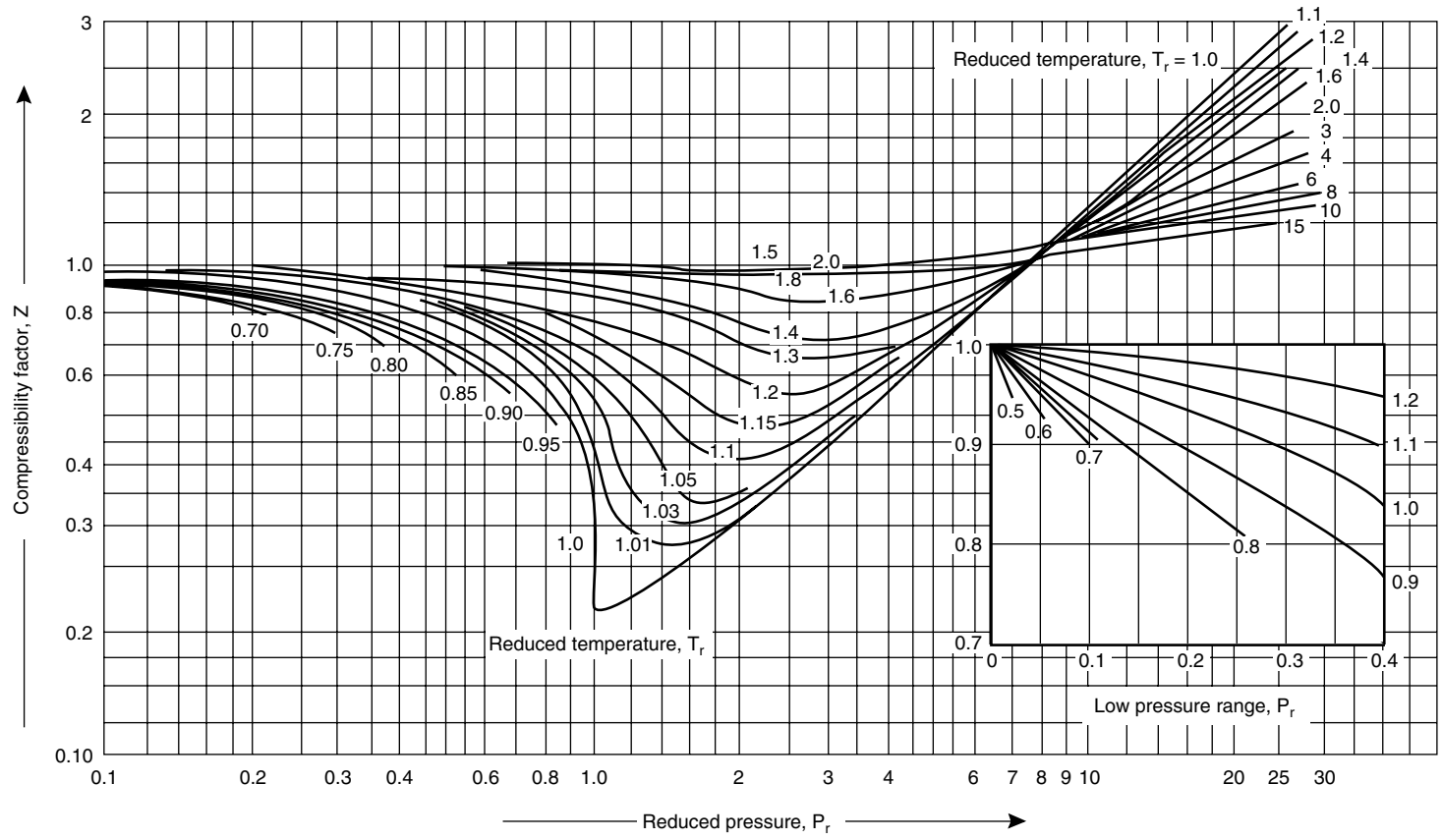


Figure 3.8. Compressibility factors of gases and vapours



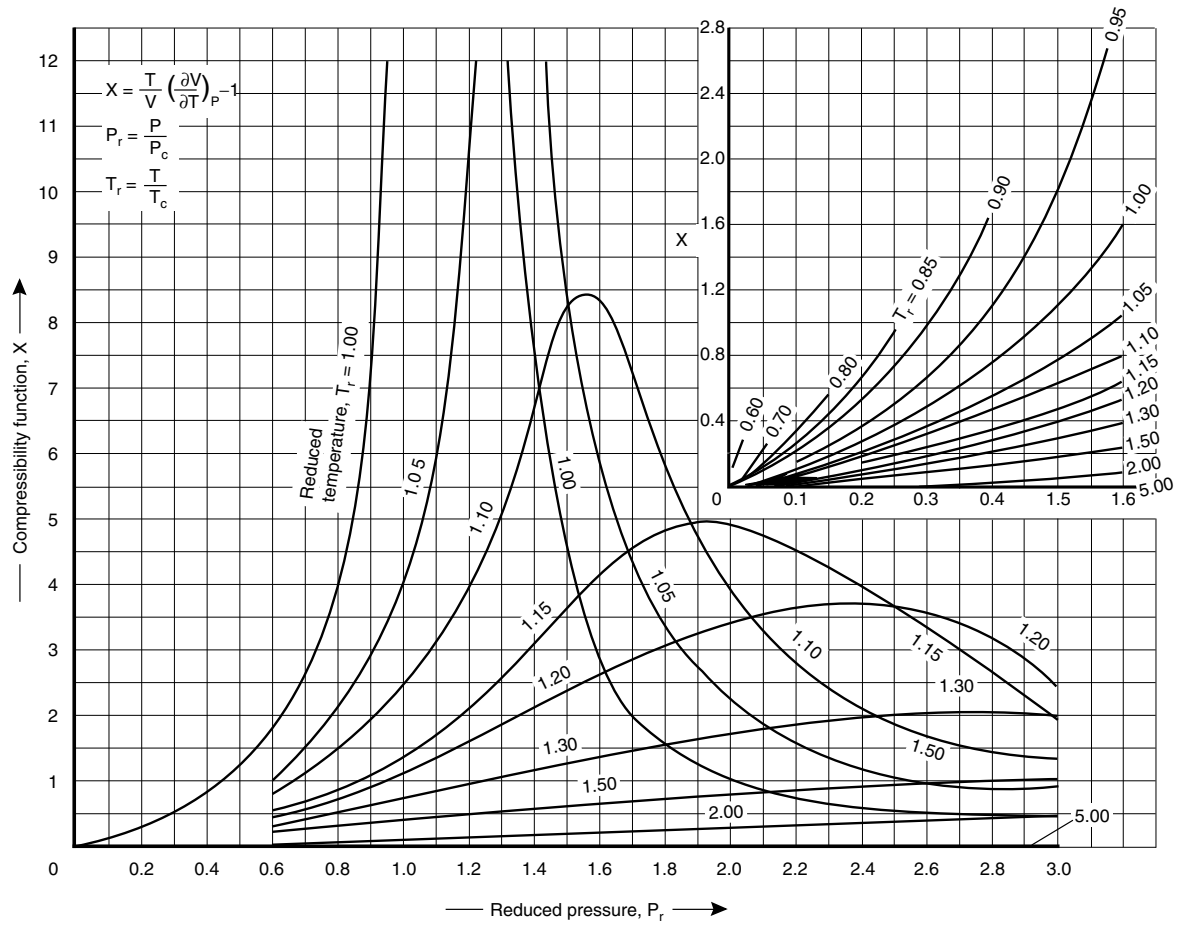


Figure 3.9. Generalised compressibility function  $X$

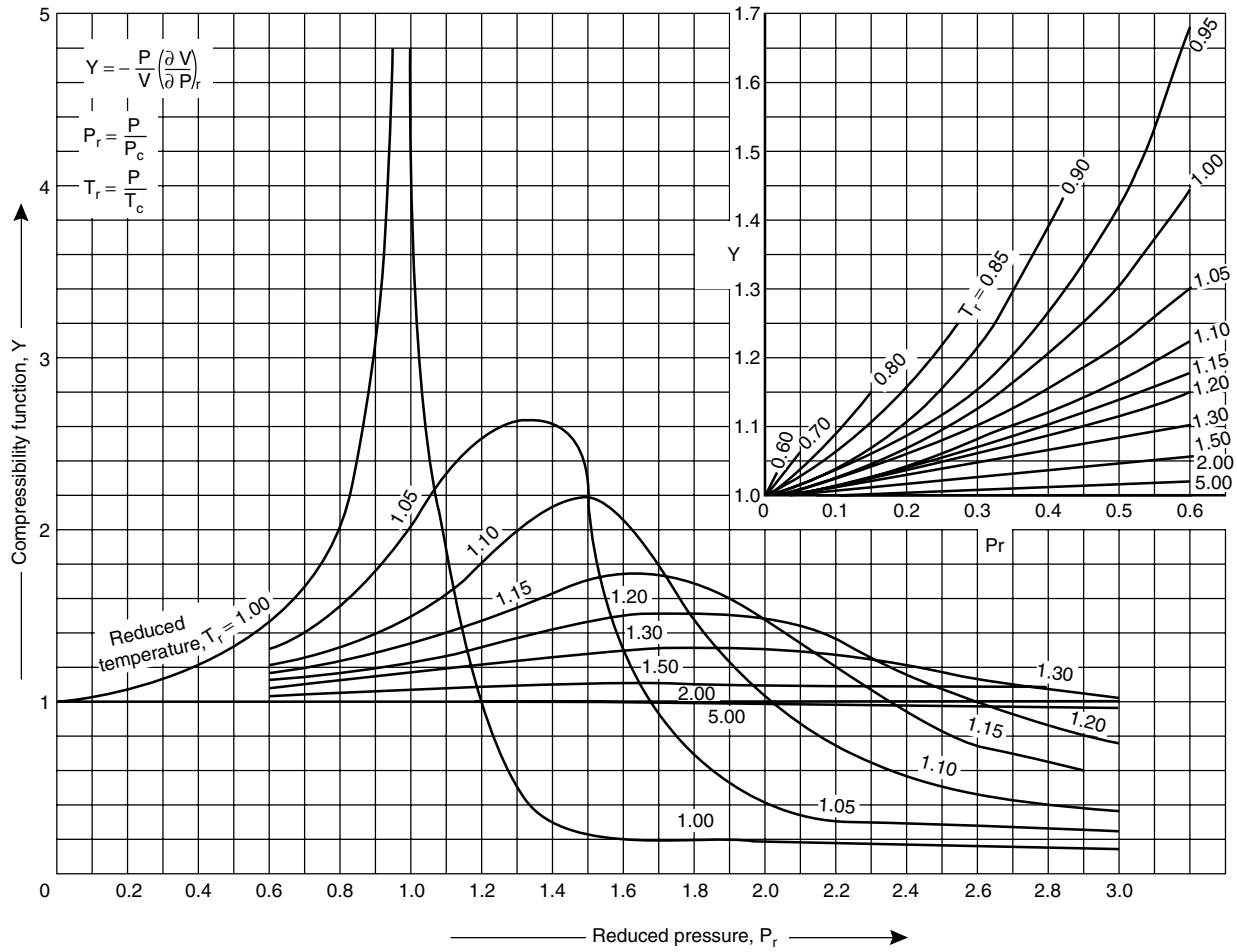


Figure 3.10. Generalised compressibility function  $Y$

TABLE 3.2. ENERGY 1, a simple energy balance program

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```

10 REM SHORT ENERGY PROGRAM, REWRITTEN IN GWBASIC, MARCH 92
20 PRINT "HEAT BALANCE PROGRAM, BASIS kmol/h, TEMP K, DATUM 298 K"
30 PRINT "INPUT THE NUMBER OF COMPONENTS, MAXIMUM 10"
40 INPUT N1
50 PRINT "INPUT HEAT CAPACITY DATA FOR EQUATION A+BT+CT^2+DT^3"
60 FOR I = 1 TO N1
70 PRINT
80 PRINT "FOR COMPONENT"; I; "INPUT A, B, C, D, INCLUDING ANY ZERO VALUES"
90 INPUT A(I), B(I), C(I), D(I)
100 NEXT I
110 H4=H5=H6=Q1=0
120 PRINT "INPUT THE NUMBER OF FEED STREAMS"
130 INPUT S1
140 FOR I = 1 TO S1
150 PRINT "FOR FEED STREAM"; I; "INPUT STREAM TEMP AND NUMBER OF COMPONENTS"
160 INPUT T1, N2
170 GOSUB 580
180 PRINT "STREAM SENSIBLE HEAT ="; H4; "kJ/h"
190 REM TOTAL SENSIBLE HEAT FEED STREAMS
200 H5 = H5 + H4
210 NEXT I
220 PRINT "INPUT NUMBER OF PRODUCT STREAMS"
230 INPUT S1
240 FOR I = 1 TO S1
250 PRINT "FOR PRODUCT STREAM"; I; "INPUT STREAM TEMP AND NUMBER OF COMPONENTS"
260 INPUT T1, N2
270 GOSUB 580
280 PRINT "STREAM SENSIBLE HEAT ="; H4; "kJ/h"
290 REM TOTAL SENSIBLE HEAT PRODUCT STREAMS
300 H6 = H6 + H4
310 NEXT I
320 PRINT "INPUT THE NUMBER OF REACTIONS AND PHASE CHANGES"
330 INPUT N4
340 IF N4 = 0 THEN 450
350 PRINT "FOR EACH REACTION OR PHASE CHANGE INPUT THE HEAT OF REACTION"
360 PRINT "OR THE LATENT HEAT, kJ/kmol; AND QUANTITY INVOLVED kmol/h"
370 PRINT "REMEMBER: HEAT ENVOLVED:POSITIVE; HEAT ABSORBED:NEGATIVE"
380 FOR I = 1 TO N4
390 PRINT
400 PRINT "NEXT REACTION/PHASE CHANGE: INPUT VALUES"
410 INPUT R, F2
420 H7 = F2*R
430 Q1 = Q1 + H7
440 NEXT I
450 REM HEAT BALANCE
460 Q = H6-H5-Q1
470 IF Q < 0 THEN 500
480 PRINT "HEATING REQUIRED ="; Q; "kJ/h"
490 GOTO 510
500 PRINT "COOLING REQUIRED ="; Q; "kJ/h"
510 PRINT "REPEAT CALCULATION WANTED ? TYPE Y FOR YES, N FOR NO"
520 INPUT P$
530 IF P$ = "N" THEN 560
540 PRINT "REPEAT CALCULATION"
550 GOTO 110
560 PRINT "CALCULATIONS FINISHED"
570 STOP
580 REM SUBROUTINE TO CALCULATE STREAM SENSIBLE HEATS
590 PRINT
600 PRINT "FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE"
610 H4 = 0
620 FOR I1 = 1 TO N2
630 PRINT "NEXT COMPONENT"
640 INPUT J, F
650 REM HEAT CAPACITY EQUATION SPLIT OVER 2 LINES
660 H1 = A(J) * (T1-298) + B(J) * (T1^2-298^2)/2
670 H2 = C(J) * (T1^3-298^3)/3 + D(J) * (T1^4-298^4)/4
680 H3 = F*(H1+H2)
690 H4 = H4+H3
700 NEXT I1
710 RETURN

```

---

### 3.13.3. Multistage compressors

Single-stage compressors can only be used for low pressure ratios. At high pressure ratios, the temperature rise will be too high for efficient operation.

To cope with the need for high pressure generation, the compression is split into a number of separate stages, with intercoolers between each stage. The interstage pressures are normally selected to give equal work in each stage.

For a two-stage compressor the interstage pressure is given by:

$$P_i = \sqrt{(P_1 \times P_2)} \quad (3.39)$$

where  $P_i$  is the intermediate-stage pressure.

#### Example 3.12

Estimate the power required to compress 1000 m<sup>3</sup>/h air from ambient conditions to 700 kN/m<sup>2</sup> gauge, using a two-stage reciprocating compressor with an intercooler.

#### Solution

Take the inlet pressure,  $P_1$ , as 1 atmosphere = 101.33 kN/m<sup>2</sup>, absolute.

Outlet pressure,  $P_2$ , = 700 + 101.33 = 801.33 kN/m<sup>2</sup>, absolute.

For equal work in each stage the intermediate pressure,  $P_i$ ,

$$= \sqrt{(1.0133 \times 10^5 \times 8.0133 \times 10^5)} = \underline{\underline{2.8495 \times 10^5}} \text{ N/m}^2$$

For air, take ratio of the specific heats,  $\gamma$ , to be 1.4.

For equal work in each stage the total work will be twice that in the first stage.

Take the inlet temperature to be 20°C, At that temperature the specific volume is given by

$$v_1 = \frac{29}{22.4} \times \frac{293}{273} = 1.39 \text{ m}^3/\text{kg}$$

$$\begin{aligned} \text{Work done, } -W &= 2 \times 1.0133 \times 10^5 \times 1.39 \times \frac{1.4}{1.4-1} \left[ \left( \frac{2.8495}{1.0133} \right)^{(1.4-1)/1.4} - 1 \right] \\ &= 338,844 \text{ J/kg} = 339 \text{ kJ/kg} \end{aligned}$$

From Figure 3.7, for a compression ratio of 2.85 the efficiency is approximately 84%. So work required

$$= 339/0.84 = \underline{\underline{404}} \text{ kJ/kg}$$

$$\text{Mass flow-rate} = \frac{1000}{1.39 \times 3600} = 0.2 \text{ kg/s}$$

$$\text{Power required} = 404 \times 0.2 = \underline{\underline{80}} \text{ kW}$$

**Example 3.13**

In the high-pressure process for the production of polyethylene, ethylene is compressed in a two-step process. In the primary step, the gas is compressed in a two-stage compressor to 25 to 30 MPa. This is followed by compression in a hypercompressor to 150 to 320 MPa.

Estimate the work required to compress ethylene to 25 MPa in a two-stage compressor. A reciprocating compressor will be used. The gas is at an initial temperature of 15°C and is cooled to 25°C after the first-stage compression.

**Solution**

As the calculations will be repetitive, use a spreadsheet.

Data  $T_{in}$  288 K  $P_{in}$  1 bar  $P_{out}$  250 ba  $R = 8.1345$  J/mol K

$T_c$  282.4 K  $P_c$  50.4 bar  $M$  28.05  $C_p$  data from Appendix D

**First stage**

Intermediate pressure  $P_2 = 15.811388$  bar eqn 3.39

Compression ratio =  $P_2/P_1 = 15.814$

$C_p$  for ethylene  $T_{in} = 288$  use eqn 3.11a

	A	B	C	D
Coeff.	3.806	0.15359	-8.35E-05	1.755E-08
$C_p$	3.806	44.23392	-6.924165	0.419256
sum, $C_p =$	41.535011			

$\gamma = C_p/(C_p - R) = 1.2502821$

From Figure 3.7, extrapolated,  $E_p = 0.86$ .

$m = 0.232768$  eqn 3.36a

$T_2 = 547.52197$  eqn 3.35

Mean temp =  $(T_1 + T_2)/2 = 417.76099$

$C_p$  at mean temp of 419.6 K

	3.806	0.15359	-8.35E-05	1.755E-08
	3.806	64.446364	-14.69784	1.2966068

sum,  $C_p = 54.851135$  kJ/kmol K

new  $\gamma = 1.1786657$

revised  $m = 0.1811049$

revised  $T_2 = 474.76117$

revised mean temp = 381.38058

little change so leave  $T_{mean}$  at 419.6 K

$T_r = T_{mean}/T_c = 1.4858357$  (1.5)

$$P_{\text{mean}} = (P_1 * P_2)/2 = 0.5$$

$$P_r = P_{\text{mean}}/P_c = 0.0099206 \quad (0.17)$$

From Figure 3.2 correction to  $C_p$  for pressure is negligible.

From Figures 3.8, 3.9, 3.10

$$Z = 1.0 \quad X = 0 \quad Y = 0$$

Essentially ideal at this pressure

$$m = 0.1762593 \quad \text{eqn 3.36a}$$

$$n = 1.2139743 \quad \text{eqn 3.38a}$$

$$-W = 303.47285 \text{ kJ/kmol} \quad \text{eqn 3.31}$$

$$\text{Actual work required} = \text{polytropic work/efficiency} = 352.87541$$

$$\text{Say } \underline{\underline{353}} \text{ kJ/kmol}$$

### *Second stage work*

As the intermediate pressure was selected to give equal work in each stage the second stage work could be taken as equal to the first stage work. This will be checked.

$$T_{\text{in}} = 298 \text{ K}$$

$$\text{compression ratio} = P_3/P_2 = 15.822785, \text{ i.e. same as first stage}$$

So, take gamma and efficiency as for first stage

$$m = 0.1811049$$

$$T_3 = 491.24593 \text{ K}$$

$$T_{\text{mean}} = 394.62296 \text{ K}$$

$C_p$  at mean temp

Coeff.	3.806	0.15359	-8.35E-05	1.755E-08
--------	-------	---------	-----------	-----------

$C_p$	3.806	60.610141	-13.00011	1.0785715
-------	-------	-----------	-----------	-----------

$$\text{sum, } C_p = 52.494599 \text{ kJ/kmol K}$$

Little change from first stage, so use same gamma and  $T_{\text{mean}}$

$$Tr = 1.5$$

$$P_{\text{mean}} = 20.4 \text{ bar}$$

$$Pr = 0.4047619 \quad (0.4)$$

From Figure 3.2 correction to  $C_p$  for pressure is approximately 2.5 J/mol.

This is less than 5 per cent, so neglect.

From Figures 3.8, 3.9, 3.10

$$Z = 1.0 \quad X = 0.1 \text{ approx.} \quad Y = 0$$

So, gas can be taken as ideal

$$-W = 314.01026 \text{ slightly higher as } T_{\text{in}} \text{ is higher}$$

$$\text{Actual work} = 365.12821 \underline{\underline{365}} \text{ kJ/kmol}$$

$$\text{Total work required first step} = \underline{\underline{718}} \text{ kJ/kmol}$$

The spreadsheet used for this example was Microsoft Works. A copy of the solution using Microsoft Excel can be found on the Butterworth-Heinemann web site: [bh.com/companions/0750641428](http://bh.com/companions/0750641428).

### 3.13.4. Electrical drives

The electrical power required to drive a compressor (or pump) can be calculated from a knowledge of the motor efficiency:

$$\text{Power} = \frac{-W \times \text{mass flow-rate}}{E_e} \quad (3.40)$$

where  $-W$  = work of compression per unit mass (equation 3.31),  
 $E_e$  = electric motor efficiency.

The efficiency of the drive motor will depend on the type, speed and size. The values given in Table 3.1 can be used to make a rough estimate of the power required.

Table 3.1. Approximate efficiencies of electric motors

Size(kW)	Efficiency (%)
5	80
15	85
75	90
200	92
750	95
>4000	97

## 3.14. ENERGY BALANCE CALCULATIONS

Energy balance calculations are best solved using spreadsheets or by writing a short computer program. A suitable program is listed in Table 3.2 and its use described below. The use of a spreadsheet is illustrated in Example 3.14b.

### Energy 1, a simple computer program

This program can be used to calculate the heat input or cooling required for a process unit, where the stream enthalpies relative to the datum temperature can be calculated from the specific heat capacities of the components (equation 3.11).

The datum temperature in the program is 25°C (298 K), which is standard for most heat of reaction data. Specific heats are represented by a cubic equation in temperature:

$$C_p = A + BT + CT^2 + DT^3$$

Any unspecified constants are typed in as zero.

If the process involves a reaction, the heat generated or consumed is computed from the heat of reaction per kmol of product (at 25°C) and the kmols of product produced.

If any component undergoes a phase change in the unit, the heat required is computed from the latent heat (at 25°C) and the quantity involved.

The component specific heat capacity coefficients, A, B, C, D, are stored as a matrix. If an energy balance is to be made on several units, the specific heat coefficients for all the components can be entered at the start, and the program rerun for each unit.

The program listing contains sufficient remark statements for the operation of the program to be easily followed. It is written in GW-BASIC for personal computers. It can easily be adapted for other forms of BASIC and for use on programmable calculators. The use of the program is illustrated in Example 3.14a. It has also been used for other examples in this chapter and in the flow-sheeting, Chapter 4.

### Example 3.14a

#### *Use of computer program ENERGY 1*

A furnace burns a liquid coal tar fuel derived from coke-ovens. Calculate the heat transferred in the furnace if the combustion gases leave at 1500 K. The burners operate with 20 per cent excess air.

Take the fuel supply temperature as 50°C (323 K) and the air temperature as 15°C (288 K).

The properties of the fuel are:

Carbon	87.5 per cent w/w
Hydrogen	8.0
Oxygen	3.5
Nitrogen	1.0
Sulphur	trace
Ash	balance
Net calorific value	39,540 kJ/kg
Latent heat of vaporisation	350 kJ/kg
Heat capacity	1.6 kJ/kg K

$C_p^\circ$  of gases, kJ/kmol K,

$$C_p = A + BT + CT^2 + DT^3$$

Component	A	B	C	D
1 CO <sub>2</sub>	19.763	7.332E-2	-5.518E-5	17.125E-9
2 H <sub>2</sub> O	32.190	19.207E-4	10.538E-6	-3.591E-9
3 O <sub>2</sub>	28.06	-3.674E-6	17.431E-6	-10.634E-9
4 N <sub>2</sub>	31.099	-1.354E-2	26.752E-6	-11.662E-9

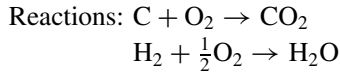
### Solution

#### *Material balance*

Basis: 100 kg (as analysis is by weight).

Assume complete combustion: maximum heat release.





Element	kg	kmol	Stoichiometric O <sub>2</sub> kmol	kmol, products
C	87.5	7.29	7.29	7.29, CO <sub>2</sub>
H <sub>2</sub>	8.0	4.0	2.0	4.0, H <sub>2</sub> O
O <sub>2</sub>	3.5	0.11	—	0.11
N <sub>2</sub>	1.0	0.04	—	0.04
Total		11.44	9.29	

O<sub>2</sub> required with 20 per cent excess =  $9.29 \times 1.2 = 11.15$  kmol.

Unreacted O<sub>2</sub> from combustion air =  $11.15 - 9.29 = 1.86$  kmol.

N<sub>2</sub> with combustion air =  $11.15 \times \frac{79}{21} = 41.94$  kmol.

Composition of combustion gases:

$$\begin{aligned} CO_2 &= 7.29 \text{ kmol} \\ H_2O &= 4.0 \\ O_2 &0.11 + 1.86 = 1.97 \\ N_2 &0.04 + 41.94 = 41.98 \end{aligned}$$

Presentation of data to the program:

$C_p$  of fuel (component 5), taken as constant,

$$A = 1.6, \quad B = C = D = 0$$

Heat of reaction and latent heat, taken to be values at datum temperature of 298 K.

There is no need to convert to kJ/kmol, providing quantities are expressed in kg. For the purposes of this example the dissociation of CO<sub>2</sub> and H<sub>2</sub>O at 1500 K is ignored.

### Computer print-out

Data inputs shown after the symbol (?)

```

RUN
HEAT BALANCE PROGRAM, BASIS kmol/h, TEMP K, DATUM 298 K
INPUT THE NUMBER OF COMPONENTS, MAXIMUM 10
? 5
INPUT HEAT CAPACITY DATA FOR EQUATION A+BT+CT^2+DT^3
FOR COMPONENT 1 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 19.763, 7.332E-2, -5.518E-5, 1.7125E-8
FOR COMPONENT 2 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 32.19, 1.9207E-3, 1.0538E-5, -3.591E-9
FOR COMPONENT 3 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 28.06, -3.67E-6, 1.74E-5, -1.0634E-8
FOR COMPONENT 4 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 31.099, -1.354E-2, 2.6752E-5, -1.1662E-8
FOR COMPONENT 5 INPUT A, B, C, D, INCLUDING ANY ZERO VALUES
? 1.6, 0 0, 0, 0

```

```

INPUT THE NUMBER OF FEED STREAMS
? 2
FOR FEED STREAM 1 INPUT STREAM TEMP AND NUMBER OF COMPONENTS
? 323, 1
FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE
NEXT COMPONENT
? 5, 100
STREAM SENSIBLE HEAT = 4000 kJ/h
FOR FEED STREAM 2 INPUT STREAM TEMP AND NUMBER OF COMPONENTS
? 288, 2
FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE
NEXT COMPONENT
? 3, 11.15
NEXT COMPONENT
? 4, 41.94
STREAM SENSIBLE HEAT = -15,484.61 kJ/h
INPUT NUMBER OF PRODUCT STREAMS
? 1
FOR PRODUCT STREAM 1 INPUT STREAM TEMP AND NUMBER OF COMPONENTS
? 1500, 4
FOR EACH COMPONENT, INPUT THE COMPONENT NUMBER AND FLOW-RATE
NEXT COMPONENT
? 1, 7.29
NEXT COMPONENT
? 2, 4.0
NEXT COMPONENT
? 3, 1.97
NEXT COMPONENT
? 4, 41.98
STREAM SENSIBLE HEAT = 2319620 kJ/h
INPUT THE NUMBER OF REACTIONS AND PHASE CHANGES
? 2
FOR EACH REACTION OR PHASE CHANGE INPUT THE HEAT OF REACTION
OR THE LATENT HEAT, kJ/kmol; AND QUANTITY INVOLVED kmol/h
REMEMBER: HEAT ENVOLED:POSITIVE; HEAT ABSORBED:NEGATIVE
NEXT REACTION/PHASE CHANGE: INPUT VALUES
? +39540, 100
NEXT REACTION/PHASE CHANGE: INPUT VALUES
? -350, 100
COOLING REQUIRED = -1587896 kJ/h
REPEAT CALCULATION WANTED ? TYPE Y FOR YES, N FOR NO
? N
CALCULATIONS FINISHED

```

Heat transferred (cooling required) = 1,590,000 kJ/100 kg

*Note:* though the program reports kJ/h, any consistent set of units can be used. For the example the basis used was 100 kg.

### ***Use of spreadsheets***

A spreadsheet can be used for repetitive calculations as a simpler alternative to writing a program. The procedure is set out below and illustrated in Example 13.14b.

From equation 13.11 the enthalpy of a stream, due to sensible heat, is given by

$$H = m \sum_{m=1}^{m=n} \int_{T_1}^{T_2} [AT + BT^2/2 + CT^3/3 + DT^4/4] \quad (13.11a)$$

where  $H$  = the stream sensible heat/enthalpy

$m$  = flowrate of the steam component kg/s or kmol/s

$n$  = number of stream components

**Procedure**

1. Set up the specific heat coefficients as a matrix.
2. Use equation 3.11a to calculate the enthalpy of each component. Tabulate the results. Sum the columns to find the total stream sensible enthalpy.
3. Repeat for all the inlet and exit streams.
4. Calculate and add the enthalpy from any reaction or phase change and add to the stream enthalpies.
5. Subtract the total enthalpy of the outlet streams from the inlet to find the change in enthalpy.

**Example 13.14b**

Repeat the calculations for the solution of Example 13.4a using a spreadsheet.

**Solution**

The spreadsheet used for this example is Microsoft Works. A copy of the example using Microsoft Excel can be found on the companion web site: <http://books.elsevier.com/companions>.

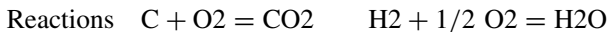
**Example 3.14b****Data**

Fuel oil	%C =	87.5	%H2 =	8	%N2 =	1
	%O2 =	3.5				
Cp kJ/kg, K	1.6 CV kJ/kg		39540	lat. heat kJ/kg		350

**Specific heats gases**

comp.	A	B	C	D	
CO2	19.763	0.0733	-5.52E-05	1.713E-08	
H2O	32.19	0.0019207	1.054E-05	-3.59E-09	
O2	28.06	-3.67E-06	1.743E-05	-1.06E-08	
N2	31.099	-0.01354	2.675E-05	-1.17E-08	
Tin fuel, K	323	Tin air, K	288	Tout, K	1500

Basis 100 kg, as analysis is by weight.

**MATERIAL BALANCE**

element	kg	kmol	stoichiometric O2, kmol	products, kmol	
C	87.5	7.29	7.29	7.29 CO2	
H2	8	4.00	2.00	4.00 H2O	
O2	3.5	0.11		0.11	
N2	1	0.04		0.04	
Totals	100	11.44	9.29	11.44	
O2 with 20% excess, kmol =			11.15	unreacted O2, kmol =	1.86
N2 with combustion air, kmol =			41.95		

Composition of combustion gases

CO2	7.29
H2O	4.00
O2	1.97
N2	41.98

ENERGY BALANCE

Take datum temp, To be 298 K

In

		mols	A	B	C	D		
Air	O2	11.15	28.06	-3.67E-06	1.743E-05	-1.06E-08		
	N2	41.95	31.099	-0.01354	2.675E-05	-1.17E-08		
	mols × Cp	O2	312.869	-4.1E-05	0.0001944	-1.19E-07		
		N2	1304.455	-0.567939	0.0011221	-4.89E-07		
	SUM		1617.324	-0.567979	0.0013165	-6.08E-07		
Energy kJ	Tin		465789.30	-23555.25	10482.593	-1045.259	total	451671.39
	To		481962.54	-25219.43	11612.883	-1198.17		467157.83
							Diff	-15486.44
Fuel	sensible heat		mass × Cp × (Tin - To) =			4000		
	combustion		mas × cv =			3954000		
			total			3958000		

Total energy in sensible + combustion: 3942513.6 kJ

Out		mols	A	B	C	D		
	CO2	7.29	19.763	0.0733	-5.52E-05	1.713E-08		
	H2O	4.00	32.19	0.0019207	1.054E-05	-3.59E-09		
	O2	1.97	28.06	-3.67E-06	1.743E-05	-1.06E-08		
	N2	41.98	31.099	-0.01354	2.675E-05	-1.17E-08		
mols × Cp	CO2		144.07227	0.534357	-0.000402	1.248E-07		
	H2O		128.76	0.0076828	4.215E-05	-1.44E-08		
	O2		55.2782	-7.24E-06	3.434E-05	-2.09E-08		
	N2		1305.536	-0.568409	0.001123	-4.9E-07		
	SUM		1633.6465	-0.026377	0.0008	-4.0E-7		
Energy	Tout		2.45E+06	-29673.72	896937.56	-506303.8	total	2811429.8
	To		486826.65	-1171.175	7032.9451	-788.6988		491899.72
							Diff	2319530.1

latent heat mass × Lv = 35000

Total out = sensible + latent = 2354530.1

Cooling required = Heat in - heat out = 1587983.5 kJ/100 kg fuel

### 3.15. UNSTEADY STATE ENERGY BALANCES

All the examples of energy balances considered previously have been for steady-state processes; where the rate of energy generation or consumption did not vary with time and the accumulation term in the general energy balance equation was taken as zero.

If a batch process is being considered, or if the rate of energy generation or removal varies with time, it will be necessary to set up a differential energy balance, similar to the differential material balance considered in Chapter 2. For batch processes the total energy requirements can usually be estimated by taking as the time basis for the calculation 1 batch; but the maximum rate of heat generation will also have to be estimated to size any heat-transfer equipment needed.

The application of a differential energy balance is illustrated in Example 3.13.

### Example 3.15

#### **Differential energy balance**

In the batch preparation of an aqueous solution the water is first heated to 80°C in a jacketed, agitated vessel; 1000 Imp. gal. (4545 kg) is heated from 15°C. If the jacket area is 300 ft<sup>2</sup> (27.9 m<sup>2</sup>) and the overall heat-transfer coefficient can be taken as 50 Btu ft<sup>-2</sup> h<sup>-1</sup> °F<sup>-1</sup> (285 W m<sup>-2</sup> K<sup>-1</sup>), estimate the heating time. Steam is supplied at 25 psig (2.7 bar).

#### **Solution**

The rate of heat transfer from the jacket to the water will be given by the following expression (see Volume 1, Chapter 9):

$$\frac{dQ}{dt} = UA(t_s - t) \quad (a)$$

where  $dQ$  is the increment of heat transferred in the time interval  $dt$ , and

$U$  = the overall-heat transfer coefficient,

$t_s$  = the steam-saturation temperature,

$t$  = the water temperature.

The incremental increase in the water temperature  $dt$  is related to the heat transferred  $dQ$  by the energy-balance equation:

$$dQ = WC_p dt \quad (b)$$

where  $WC_p$  is the heat capacity of the system.

Equating equations (a) and (b)

$$WC_p \frac{dt}{dt} = UA(t_s - t)$$

Integrating 
$$\int_0^{t_B} dt = \frac{WC_p}{UA} \int_{t_1}^{t_2} \frac{dt}{(t_s - t)}$$

Batch heating time

$$t_B = -\frac{WC_p}{UA} \ln \frac{t_s - t_2}{t_s - t_1}$$

For this example  $WC_p = 4.18 \times 4545 \times 10^3 \text{ JK}^{-1}$

$$UA = 285 \times 27 \text{ WK}^{-1}$$

$$t_1 = 15^\circ\text{C}, \quad t_2 = 80^\circ\text{C}, \quad t_s = 130^\circ\text{C}$$

$$\begin{aligned} t_B &= -\frac{4.18 \times 4545 \times 10^3}{285 \times 27.9} \ln \frac{130 - 80}{130 - 15} \\ &= 1990\text{s} = \underline{\underline{33.2 \text{ min}}} \end{aligned}$$

In this example the heat capacity of the vessel and the heat losses have been neglected for simplicity. They would increase the heating time by 10 to 20 per cent.

### 3.16. ENERGY RECOVERY

Process streams at high pressure or temperature, and those containing combustible material, contain energy that can be usefully recovered. Whether it is economic to recover the energy content of a particular stream will depend on the value of the energy that can be usefully extracted and the cost of recovery. The value of the energy will depend on the primary cost of energy at the site. It may be worth while recovering energy from a process stream at a site where energy costs are high but not where the primary energy costs are low. The cost of recovery will be the capital and operating cost of any additional equipment required. If the savings exceed the operating cost, including capital charges, then the energy recovery will usually be worthwhile. Maintenance costs should be included in the operating cost (see Chapter 6).

Some processes, such as air separation, depend on efficient energy recovery for economic operation, and in all processes the efficient utilisation of energy recovery techniques will reduce product cost.

Some of the techniques used for energy recovery in chemical process plants are described briefly in the following sections. The references cited give fuller details of each technique. Miller (1968) gives a comprehensive review of process energy systems; including heat exchange, and power recover from high-pressure fluid streams.

Kenney (1984) reviews the application of thermodynamic principles to energy recovery in the process industries.

#### 3.16.1. Heat exchange

The most common energy-recovery technique is to utilise the heat in a high-temperature process stream to heat a colder stream: saving steam costs; and also cooling water, if the hot stream requires cooling. Conventional shell and tube exchangers are normally used. More total heat-transfer area will be needed, over that for steam heating and water cooling, as the overall driving forces will be smaller.

The cost of recovery will be reduced if the streams are located conveniently close.

The amount of energy that can be recovered will depend on the temperature, flow, heat capacity, and temperature change possible, in each stream. A reasonable temperature driving force must be maintained to keep the exchanger area to a practical size. The most efficient exchanger will be the one in which the shell and tube flows are truly countercurrent. Multiple tube pass exchangers are usually used for practical reasons. With multiple tube passes the flow will be part counter-current and part co-current and temperature crosses can occur, which will reduce the efficiency of heat recovery (see Chapter 12).

The hot process streams leaving a reactor or a distillation column are frequently used to preheat the feedstreams.

#### 3.16.2. Heat-exchanger networks

In an industrial process there will be many hot and cold streams and there will be an optimum arrangement of the streams for energy recovery by heat exchange. The problem of synthesising a network of heat exchangers has been studied by many workers,

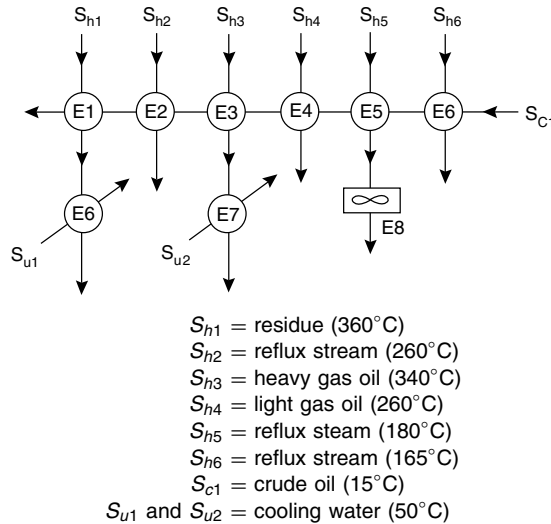


Figure 3.11. Typical heat-exchanger network

particularly in respect of optimising heat recovery in crude petroleum distillation. An example of crude preheat train is shown in Figure 3.11. The general problem of the synthesis and optimisation of a network of heat exchangers has been defined by Masso and Rudd (1969).

Consider that there are  $M$  hot streams,  $S_{hi}$  ( $i = 1, 2, 3, \dots, M$ ) to be cooled and  $N$  cold streams  $S_{cj}$  ( $j = 1, 2, 3, \dots, N$ ) to be heated; each stream having an inlet temperature  $t_f$ , or an outlet temperature  $t_0$ , and a stream heat capacity  $W_i$ . There may also be  $S_{uk}$  ( $k = 1, 2, 3, \dots, L$ ) auxiliary steam heated or water-cooled exchangers.

The problem is to create a minimum cost network of exchangers, that will also meet the design specifications on the required outlet temperature  $t_0$  of each stream. If the strictly mathematical approach is taken of setting up all possible arrangements and searching for the optimum, the problem, even for a small number of exchangers, would require an inordinate amount of computer time. Boland and Linnhoff (1979) point out that for a process with four cold and three hot streams,  $2.4 \times 10^{18}$  arrangements are possible. Most workers have taken a more pragmatic, "heuristic", approach to the problem, using "rules of thumb" to generate a limited number of feasible networks, which are then evaluated.

Porton and Donaldson (1974) suggest a simple procedure that involves the repeated matching of the hottest stream (highest  $t_f$ ) against the cold stream with the highest required outlet temperature (highest  $t_0$ ).

A general survey of computer and manual methods for optimising exchanger networks is given by Nishida *et al.* (1977); see also Sirola (1974).

The design of heat exchanger networks is covered in more detail in Section 3.17.

### 3.16.3. Waste-heat boilers

If the process streams are at a sufficiently high temperature the heat recovered can be used to generate steam.

Waste-heat boilers are often used to recover heat from furnace flue gases and the process gas streams from high-temperature reactors. The pressure, and superheat temperature, of the stream generated will depend on the temperature of the hot stream and the approach temperature permissible at the boiler exit (see Chapter 12). As with any heat-transfer equipment, the area required will increase as the mean temperature driving force (log mean  $\Delta T$ ) is reduced. The permissible exit temperature may also be limited by process considerations. If the gas stream contains water vapour and soluble corrosive gases, such as HCl or SO<sub>2</sub>, the exit gases temperature must be kept above the dew point.

Hinchley (1975) discusses the design and operation of waste heat boilers for chemical plant. Both fire tube and water tube boilers are used. A typical arrangement of a water tube boiler on a reformer furnace is shown in Figure 3.12 and a fire tube boiler in Figure 3.13. The application of a waste-heat boiler to recover energy from the reactor exit streams in a nitric acid plant is shown in Figure 3.14.

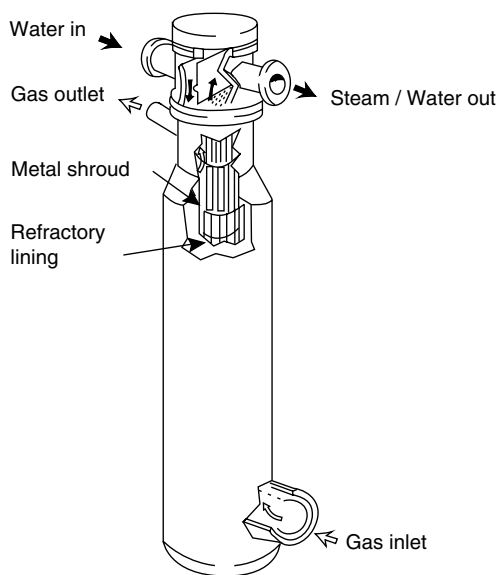


Figure 3.12. Reformed gas waste-heat boiler arrangement of vertical U-tube water-tube boiler (Reprinted by permission of the Council of the Institution of Mechanical Engineers from the Proceedings of the Conference on Energy Recovery in the Process Industries, London, 1975.)

The selection and operation of waste heat boilers for industrial furnaces is discussed in the *Efficient Use of Energy*, Dryden (1975).

#### 3.16.4. High-temperature reactors

If a reaction is highly exothermic, cooling will be needed and, if the reactor temperature is high enough, the heat removed can be used to generate steam. The lowest steam pressure normally used in the process industries is 2.7 bar (25 psig) and steam is normally



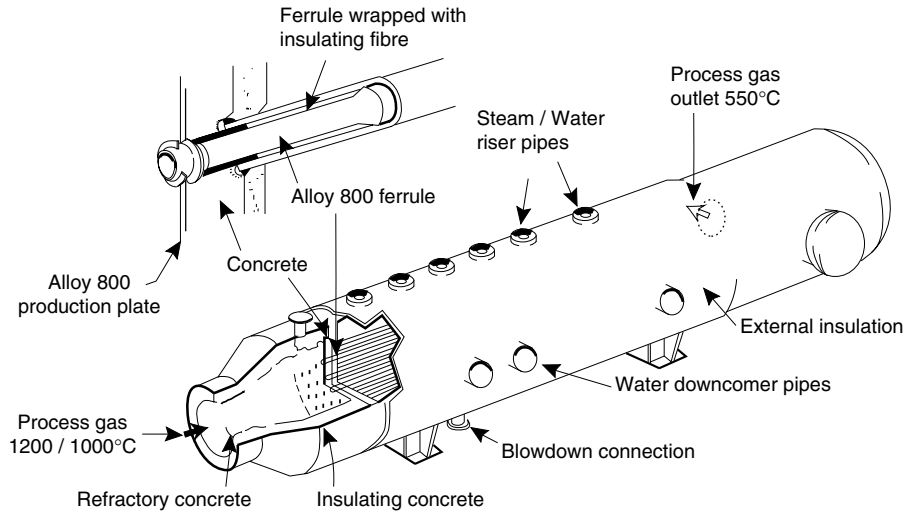
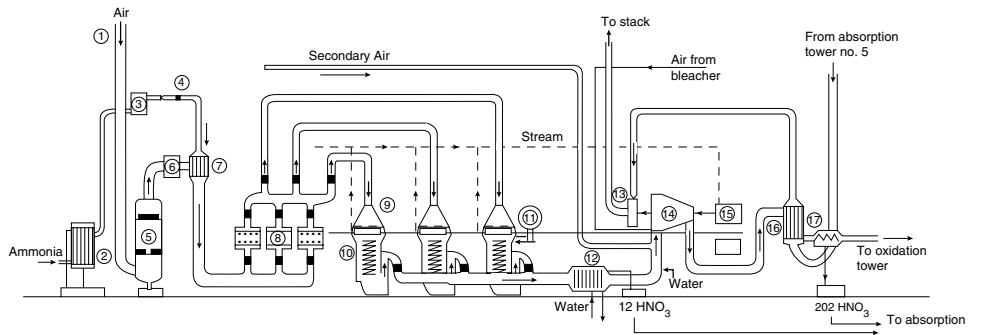


Figure 3.13. Reformed gas waste-heat boiler, principal features of typical natural circulation fire-tube boilers (Reprinted by permission of the Council of the Institution of Mechanical Engineers from the Proceedings of the Conference on Energy Recovery in the Process Industries, London, 1975.)



- |                        |                  |                      |                      |
|------------------------|------------------|----------------------|----------------------|
| 1. Air entry           | 6. Air preheater | 10. Lamont boilers   | 14. Compressor       |
| 2. Ammonia vaporiser   | 7. Gas mixer     | 11. Steam drum       | 15. Steam turbine    |
| 3. Ammonia filter      | 8. Gas filters   | 12. Gas cooler No. 1 | 16. Heat exchanger   |
| 4. Control valves      | 9. Converters    | 13. Exhaust turbine  | 17. Gas cooler No. 2 |
| 5. Air-scrubbing tower |                  |                      |                      |

(From *Nitric Acid Manufacture*, Miles (1961), with permission)

Figure 3.14. Connections of a nitric acid plant, intermediate pressure type

distributed at a header pressure of around 8 bar (100 psig); so any reactor with a temperature above 200°C is a potential steam generator.

Three systems are used:

1. Figure 3.15a. An arrangement similar to a conventional water-tube boiler. Steam is generated in cooling pipes within the reactor and separated in a steam drum.

2. Figure 3.15*b*. Similar to the first arrangement but with the water kept at high pressure to prevent vaporisation. The high-pressure water is flashed to steam at lower pressure in a flash drum. This system would give more responsive control of the reactor temperature.
3. Figure 3.15*c*. In this system a heat-transfer fluid, such as Dowtherm (see Perry and Green (1984) and Singh (1985) for details of heat-transfer fluids), is used to avoid the need for high-pressure tubes. The steam is raised in an external boiler.

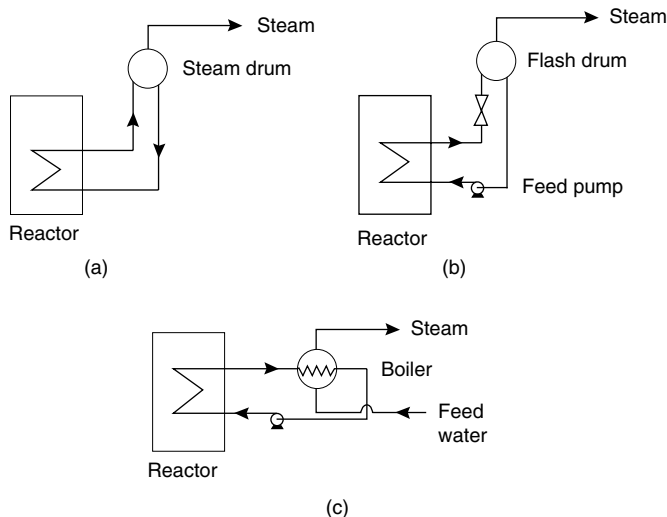


Figure 3.15. Steam generation

### 3.16.5. Low-grade fuels

The waste products from any process (gases, liquids and solids) which contain significant quantities of combustible material can be used as low-grade fuels; for raising steam or direct process heating. Their use will only be economic if the intrinsic value of the fuel justifies the cost of special burners and other equipment needed to burn the waste. If the combustible content of the waste is too low to support combustion, the waste will have to be supplemented with higher calorific value primary fuels.

#### **Reactor off-gases**

The off-gases (vent gas) from reactors, and recycle stream purges are often of high enough calorific value to be used as fuels.

The calorific value of a gas can be calculated from the heats of combustion of its constituents; the method is illustrated in Example 3.14.

Other factors which, together with the calorific value, will determine the economic value of an off-gas as a fuel are the quantity available and the continuity of supply. Waste gases are best used for steam raising, rather than for direct process heating, as this decouples the source from the use and gives greater flexibility.

**Example 3.16***Calculation of a waste-gas calorific value*

The typical vent-gas analysis from the recycle stream in an oxyhydrochlorination process for the production of dichloroethane (DCE) (British patent BP 1,524,449) is given below, percentages on volume basis.

O<sub>2</sub> 7.96, CO<sub>2</sub> + N<sub>2</sub> 87.6, CO 1.79, C<sub>2</sub>H<sub>4</sub> 1.99, C<sub>2</sub>H<sub>6</sub> 0.1, DCE 0.54

Estimate the vent gas calorific value.

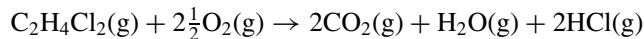
**Solution**

Component calorific values, from Perry and Chilton (1973)

CO	67.6 kcal/mol	=	283 kJ/mol
C <sub>2</sub> H <sub>4</sub>	372.8	=	1560.9
C <sub>2</sub> H <sub>6</sub>	337.2	=	1411.9

The value for DCE can be estimated from the heats of formation.

Combustion reaction:



$\Delta H_f^\circ$  from Appendix D

$$\begin{aligned} \text{CO}_2 &= -393.8 \text{ kJ/mol} \\ \text{H}_2\text{O} &= -242.0 \\ \text{HCl} &= -92.4 \\ \text{DCE} &= -130.0 \\ \Delta H_c^\circ &= \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants} \\ &= [2(-393.8) - 242.0 + 2(-92.4)] - [-130.0] \\ &= \underline{\underline{-1084.4 \text{ kJ}}} \end{aligned}$$

Estimation of vent gas c.v., basis 100 mols.

Component	mols/100 mols		Calorific value (kJ/mol)		Heating value
CO	1.79	×	283.0	=	506.6
C <sub>2</sub> H <sub>4</sub>	1.99		1560.9		3106.2
C <sub>2</sub> H <sub>6</sub>	0.1		1411.9		141.2
DCE	0.54		1084.4		585.7
Total					4339.7

$$\begin{aligned} \text{Calorific value of vent gas} &= \frac{4339.7}{100} = 43.4 \text{ kJ/mol} \\ &= \frac{43.4}{22.4} \times 10^3 = \underline{\underline{1938 \text{ kJ/m}^3}} (52 \text{ Btu/ft}^3) \text{ at 1 bar, } 0^\circ\text{C} \end{aligned}$$

Barely worth recovery, but if the gas has to be burnt to avoid pollution it could be used in an incinerator such as that shown in Figure 3.16, giving a useful steam production to offset the cost of disposal.

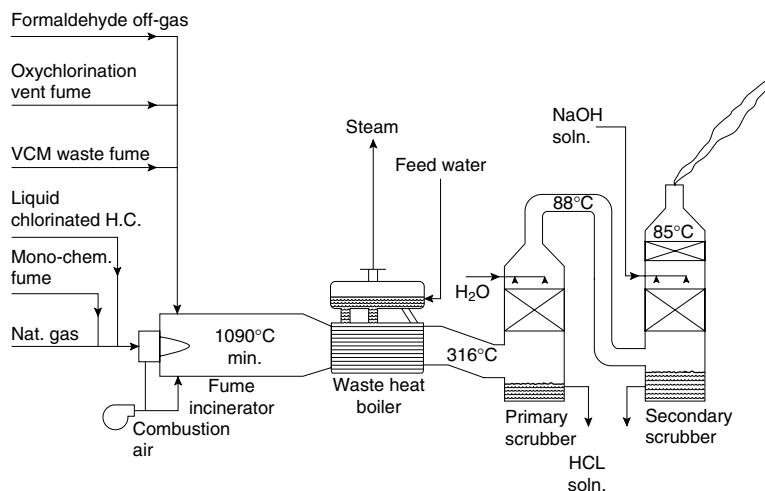


Figure 3.16. Typical incinerator-heat recovery-scrubber system for vinyl-chloride-monomer process waste (Courtesy of John Thurley Ltd.)

### **Liquid and solid wastes**

Combustible liquid and solid waste can be disposed of by burning, which is usually preferred to dumping. Incorporating a steam boiler in the incinerator design will enable an otherwise unproductive, but necessary operation, to save energy. If the combustion products are corrosive, corrosion-resistant materials will be needed, and the flue gases scrubbed to reduce air pollution. An incinerator designed to handle chlorinated and other liquid and solid wastes is shown in Figure 3.16. This incinerator incorporates a steam boiler and a flue-gas scrubber. The disposal of chlorinated wastes is discussed by Santoleri (1973).

Dunn and Tomkins (1975) discuss the design and operation of incinerators for process wastes. They give particular attention to the need to comply with the current clean-air legislation, and the problem of corrosion and erosion of refractories and heat-exchange surfaces.

#### **3.16.6. High-pressure process streams**

Where high-pressure gas or liquid process streams are throttled to lower pressures, energy can be recovered by carrying out the expansion in a suitable turbine.

### **Gas streams**

The economic operation of processes which involve the compression and expansion of large quantities of gases, such as ammonia synthesis, nitric acid production and air

separation, depends on the efficient recovery of the energy of compression. The energy recovered by expansion is often used to drive the compressors directly; as shown in Figure 3.14. If the gas contains condensible components it may be advisable to consider heating the gas by heat exchange with a higher temperature process stream before expansion. The gas can then be expanded to a lower pressure without condensation and the power generated increased.

An interesting process incorporating an expansion turbine is described by Barlow (1975) who discusses energy recovery in an organic acids plant (acetic and propionic). In this process a thirteen-stage turbo-expander is used to recover energy from the off-gases. The pressure range is deliberately chosen to reduce the off-gases to a low temperature at the expander outlet ( $-60^{\circ}\text{C}$ ), for use for low-temperature cooling, saving refrigeration.

The energy recoverable from the expansion of a gas can be estimated by assuming polytropic expansion; see Section 3.13.2 and Example 3.17.

The design of turboexpanders for the process industries is discussed by Bloch *et al.* (1982).

### Example 3.17

Consider the extraction of energy from the tail gases from a nitric acid adsorption tower, such as that described in Chapter 4, Example 4.4.

Gas composition, kmol/h:

O <sub>2</sub>	371.5
N <sub>2</sub>	10,014.7
NO	21.9
NO <sub>2</sub>	Trace
H <sub>2</sub> O	saturated at 250°C

If the gases leave the tower at 6 atm, 25°C, and are expanded to, say, 1.5 atm, calculate the turbine exit gas temperatures without preheat, and if the gases are preheated to 400°C with the reactor off-gas. Also, estimate the power recovered from the preheated gases.

### Solution

For the purposes of this calculation it will be sufficient to consider the tail gas as all nitrogen, flow 10,410 kmol/h.

$$P_c = 33.5 \text{ atm}, \quad T_c = 126.2 \text{ K}$$

Figure 3.6 can be used to estimate the turbine efficiency.

$$\begin{aligned} \text{Exit gas volumetric flow-rate} &= \frac{10,410}{3600} \times 22.4 \times \frac{1}{1.5} \\ &\simeq 43 \text{ m}^3/\text{s} \end{aligned}$$

from Figure 3.6  $E_p = 0.75$

$$P_r \text{ inlet} = \frac{6}{33.5} = 0.18$$

$$T_r \text{ inlet} = \frac{298}{126.2} = 2.4$$

For these values the simplified equations can be used, equations 3.37a and 3.38a.

For  $N_2$   $\gamma = 1.4$

$$m = \frac{1.4 - 1}{1.4} \times 0.75 = 0.21$$

$$n = \frac{1}{1 - m} = \frac{1}{1 - 0.21} = 1.27$$

$$\text{without preheat } T_2 = 298 \left( \frac{1.5}{6.0} \right)^{0.21} = 223 \text{ K}$$

$$= \underline{\underline{-50^\circ\text{C}}} \text{ (acidic water would condense out)}$$

$$\text{with preheat } T_2 = 673 \left( \frac{1.5}{6.0} \right)^{0.21} = 503 \text{ K}$$

$$= \underline{\underline{230^\circ\text{C}}}$$

From equation 3.31, work done by gases as a result of polytropic expansion

$$= -1 \times 673 \times 8.314 \times \frac{1.27}{1.27 - 1} \left\{ \left( \frac{1.5}{6.0} \right)^{(1.27-1)/1.27} - 1 \right\}$$

$$= 6718 \text{ kJ/kmol}$$

$$\text{Actual work} = \text{polytropic work} \times E_p$$

$$= 6718 \times 0.75 = \underline{\underline{5039 \text{ kJ/kmol}}}$$

$$\text{Power output} = \text{work/kmol} \times \text{kmol/s} = 5039 \times \frac{10,410}{3600}$$

$$= 14,571 \text{ kJ/s} = \underline{\underline{14.6 \text{ MW}}}$$

### **Liquid streams**

As liquids are essentially incompressible, less energy is stored in a compressed liquid than a gas. However, it is worth considering power recovery from high-pressure liquid streams (>15 bar) as the equipment required is relatively simple and inexpensive. Centrifugal pumps are used as expanders and are often coupled directly to pumps. The design, operation and cost of energy recovery from high-pressure liquid streams is discussed by Jenett (1968), Chada (1984) and Buse (1985).

### 3.16.7. Heat pumps

A heat pump is a device for raising low grade heat to a temperature at which the heat can be utilised. It pumps the heat from a low temperature source to the higher temperature sink, using a small amount of energy relative to the heat energy recovered.

Heat pumps are increasingly finding applications in the process industries. A typical application is the use of the low grade heat from the condenser of a distillation column to provide heat for the reboiler; see Barnwell and Morris (1982) and Meili (1990). Heat pumps are also used with dryers, heat being abstracted from the exhaust air and used to preheat the incoming air. The use of a heat pump with an evaporator is described in Volume 2, Chapter 14.

Details of the thermodynamic cycles used for heat pumps can be found in most textbooks on Engineering Thermodynamics, and in Reay and MacMichael (1988). In the process industries heat pumps operating on the mechanical vapour compression cycle would normally be used. A vapour compression heat pump applied to a distillation column is shown in Figure 3.17*a*. The working fluid, usually a commercial refrigerant, is fed to the reboiler as a vapour at high pressure and condenses, giving up heat to vaporise the process fluid. The liquid refrigerant from the reboiler is then expanded over a throttle valve and the resulting wet vapour fed to the column condenser. In the condenser the wet refrigerant is dried, taking heat from the condensing process vapour. The refrigerant vapour is then compressed and recycled to the reboiler, completing the working cycle.

If the conditions are suitable the process fluid can be used as the working fluid for the heat pump. This arrangement is shown in Figure 3.17*b*. The hot process liquid at high

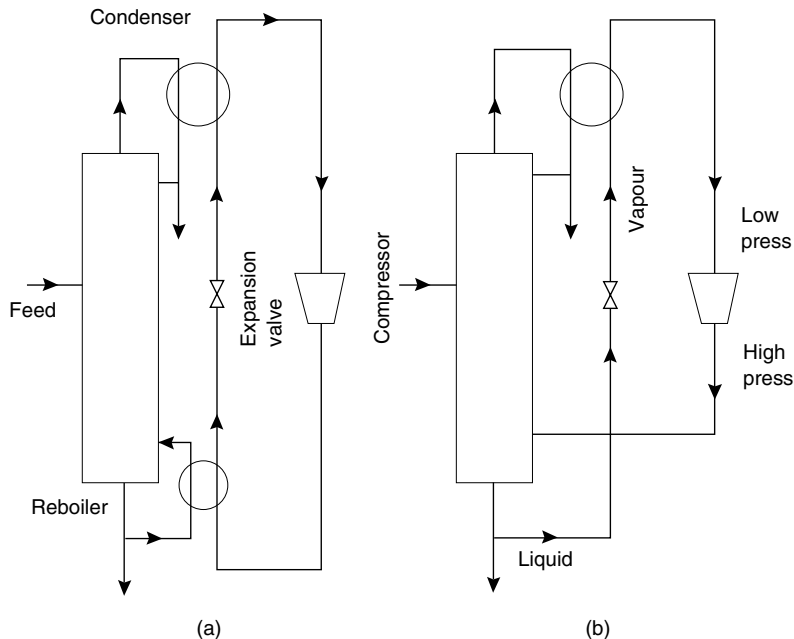


Figure 3.17. Distillation column with heat pump (a) Separate refrigerant circuit (b) Using column fluid as the refrigerant

pressure is expanded over the throttle valve and fed to the condenser, to provide cooling to condense the vapour from the column. The vapour from the condenser is compressed and returned to the base of the column. In an alternative arrangement, the process vapour is taken from the top of the column, compressed and fed to the reboiler to provide heating.

The “efficiency” of a heat pump is measured by the coefficient of performance,  $COP$ :

$$COP = \frac{\text{energy delivered at higher temperature}}{\text{energy input compressor}}$$

The  $COP$  will depend principally on the working temperatures.

The economics of the application of heat pumps in the process industries is discussed by Holland and Devotta (1986). Details of the application of heat pumps in a wide range of industries are given by Moser and Schnitzer (1985).

### 3.17. PROCESS INTEGRATION AND PINCH TECHNOLOGY

Process integration can lead to a substantial reduction in the energy requirements of a process. In recent years much work has been done on developing methods for investigating energy integration and the efficient design of heat exchanger networks; see Gundersen and Naess (1988). One of the most successful and generally useful techniques is that developed by Bodo Linnhoff and other workers: *pinch technology*. The term derives from the fact that in a plot of the system temperatures versus the heat transferred, a *pinch* usually occurs between the hot stream and cold stream curves, see Figure 3.22. It has been shown that the pinch represents a distinct thermodynamic break in the system and that, for minimum energy requirements, heat should not be transferred across the pinch, Linnhoff and Townsend (1982).

In this section the fundamental principles of the pinch technology method for energy integration will be outlined and illustrated with reference to a simple problem. The method and its applications are described fully in a guide published by the Institution of Chemical Engineers, IChemE (1994); see also Douglas (1988).

#### 3.17.1. Pinch technology

The development and application of the method can be illustrated by considering the problem of integrating the utilisation of energy between 4 process streams. Two hot streams which require cooling, and two cold streams that have to be heated. The process data for the streams is set out in Table 3.3. Each stream starts from a source temperature  $T_s$ , and is to be heated or cooled to a target temperature  $T_t$ . The heat capacity of each stream is shown as  $CP$ . For streams where the specific heat capacity can be taken as constant, and there is no phase change,  $CP$  will be given by:

$$CP = mCp$$

where  $m$  = mass flow-rate, kg/s

$Cp$  = average specific heat capacity between  $T_s$  and  $T_t$  kJ kg<sup>-1</sup>°C<sup>-1</sup>



Table 3.3. Data for heat integration problem

Stream number	Type	Heat capacity CP, kW/°C	$T_s$ °C	$T_t$ °C	Heat load kW
1	hot	3.0	180	60	360
2	hot	1.0	150	30	120
3	cold	2.0	20	135	230
4	cold	4.5	80	140	270

The heat load shown in the table is the total heat required to heat, or cool, the stream from the source to target temperature.

The four streams are shown diagrammatically below, Figure 3.18:

There is clearly scope for energy integration between these four streams. Two require heating and two cooling; and the stream temperatures are such that heat can be transferred from the hot to the cold streams. The task is to find the best arrangement of heat exchangers to achieve the target temperatures.

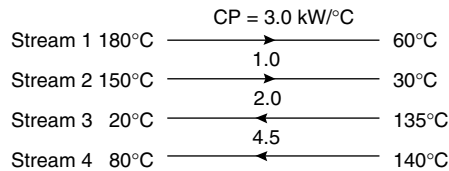


Figure 3.18. Diagrammatic representation of process streams

### Simple two-stream problem

Before investigating the energy integration of the four streams shown in Table 3.3, the use of a temperature-enthalpy diagram will be illustrated for a simple problem involving only two streams. The general problem of heating and cooling two streams from source to target temperatures is shown in Figure 3.19. Some heat is exchanged between the streams in the heat exchanger. Additional heat, to raise the cold stream to the target temperature, is provided by the hot utility (usually steam) in the heater; and additional cooling to bring the hot stream to its target temperature, by the cold utility (usually cooling water) in the cooler.

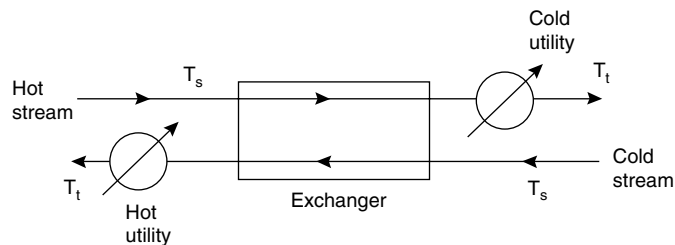


Figure 3.19. Two-stream exchanger problem

In Figure 3.20 the stream temperatures are plotted on the y-axis and the enthalpy change in each stream on the x-axis. For heat to be exchanged a minimum temperature difference must be maintained between the two streams. This is shown as  $\Delta T_{\min}$  on the diagram. The practical minimum temperature difference in a heat exchanger will usually be between 10 and 20°C; see Chapter 12.

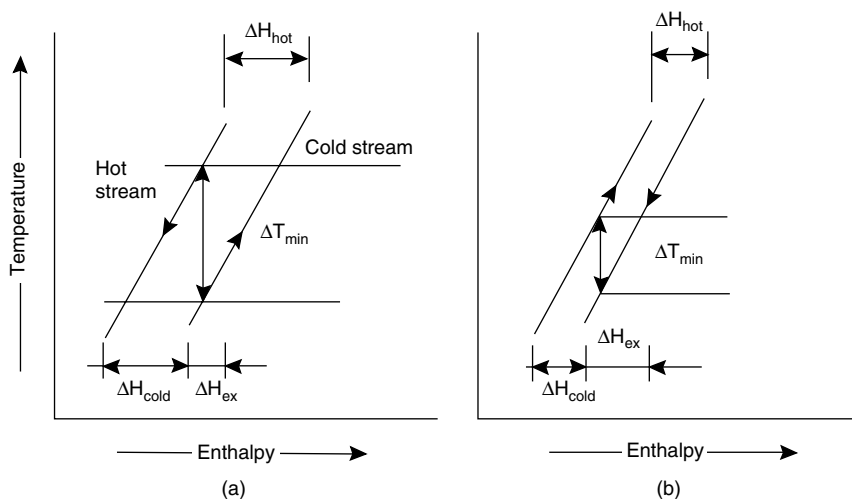


Figure 3.20. Temperature-enthalpy for 2-stream example

The heat transferred between the streams is shown on the diagram as  $\Delta H_{\text{ex}}$ , and the heat transferred from the utilities as  $\Delta H_{\text{cold}}$  and  $\Delta H_{\text{hot}}$ :

$$\Delta H = CP \times (\text{temperature change})$$

It can be seen by comparing Figure 3.20a and b that the amount of heating and cooling needed will depend on the minimum temperature difference. Decreasing  $\Delta T_{\min}$  will increase the amount of heat exchanged between the two streams and so decrease the consumption of the hot and cold utilities.

### Four stream problem

In Figure 3.21a the hot streams given in Table 3.3 are shown plotted on a temperature-enthalpy diagram.

As the diagram shows changes in the enthalpy of the streams, it does not matter where a particular curve is plotted on the enthalpy axis; as long as the curve runs between the correct temperatures. This means that where more than one stream appears in a temperature interval, the stream heat capacities can be added to give the composite curve shown in Figure 3.21b.

In Figure 3.22, the composite curve for the hot streams and the composite curve for cold streams are drawn with a minimum temperature difference, the displacement between the curves, of 10°C. This implies that in any of the exchangers to be used in the network the temperature difference between the streams will not be less than 10°C.

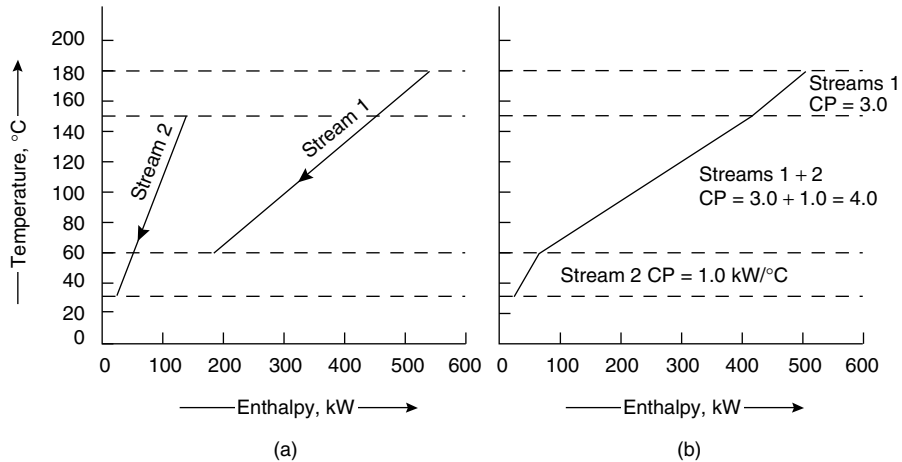


Figure 3.21. Hot stream temperature v. enthalpy (a) Separate hot streams (b) Composite hot streams

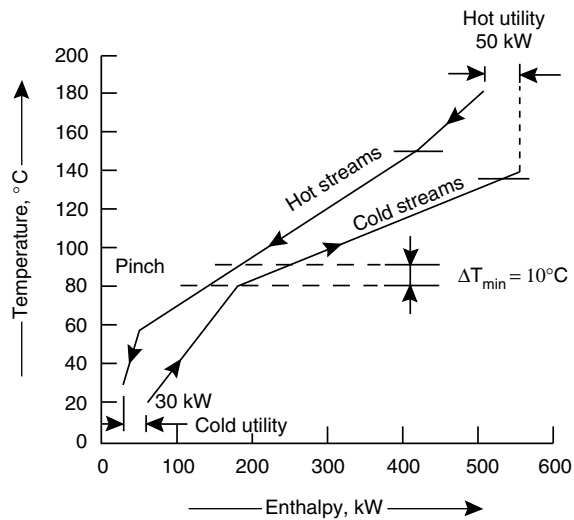


Figure 3.22. Hot and cold stream composite curves

As for the two-stream problem, the displacement of the curves at the top and bottom of the diagram gives the hot and cold utility requirements. These will be the minimum values needed to satisfy the target temperatures. This is valuable information. It gives the designer target values for the utilities to aim for when designing the exchanger network. Any design can be compared with the minimum utility requirements to check if further improvement is possible.

In most exchanger networks the minimum temperature difference will occur at only one point. This is termed the *pinch*. In the problem being considered, the pinch occurs at between  $90^{\circ}\text{C}$  on the hot stream curve and  $80^{\circ}\text{C}$  on the cold stream curve.

**Significance of the pinch**

The pinch divides the system into two distinct thermodynamic regions. The region above the pinch can be considered a heat sink, with heat flowing into it, from the hot utility, but not out of it. Below the pinch the converse is true. Heat flows out of the region to the cold utility. No heat flows across the pinch.

If a network is designed that requires heat to flow across the pinch, then the consumption of the hot and cold utilities will be greater than the minimum values that could be achieved.

**3.17.2. The problem table method**

The problem table is the name given by Linnhoff and Flower to a numerical method for determining the pinch temperatures and the minimum utility requirements; Linnhoff and Flower (1978). Once understood, it is the preferred method, avoiding the need to draw the composite curves and manoeuvre the composite cooling curve using, for example, tracing paper or cut-outs, to give the chosen minimum temperature difference on the diagram. The procedure is as follows:

1. Convert the actual stream temperatures  $T_{act}$  into interval temperatures  $T_{int}$  by subtracting half the minimum temperature difference from the hot stream temperatures, and by adding half to the cold stream temperatures:

$$\begin{aligned} \text{hot streams } T_{int} &= T_{act} - \frac{\Delta T_{min}}{2} \\ \text{cold streams } T_{int} &= T_{act} + \frac{\Delta T_{min}}{2} \end{aligned}$$

The use of the interval temperature rather than the actual temperatures allows the minimum temperature difference to be taken into account.  $\Delta T_{min} = 10^\circ\text{C}$  for the problem being considered; see Table 3.4.

Table 3.4. Interval temperatures for  $\Delta T_{min} = 10^\circ\text{C}$

Stream	Actual temperature		Interval temperature	
1	180	60	175	55
2	150	30	145	25
3	20	135	(25)	140
4	80	140	85	(145)

2. Note any duplicated interval temperatures. These are bracketed in Table 3.4.
3. Rank the interval temperatures in order of magnitude, showing the duplicated temperatures only once in the order; see Table 3.5.
4. Carry out a heat balance for the streams falling within each temperature interval:  
For the nth interval:

$$\Delta H_n = (\Sigma CP_c - \Sigma CP_h) (\Delta T_n)$$

where  $\Delta H_n$  = net heat required in the nth interval

$\Sigma CP_c$  = sum of the heat capacities of all the cold streams in the interval

$\Sigma CP_h$  = sum of the heat capacities of all the hot streams in the interval

$\Delta T_n$  = interval temperature difference =  $(T_{n-1} - T_n)$

See Table 3.6.

Table 3.5. Ranked order of interval temperatures

Rank	Interval $\Delta T_n$ °C	Streams in interval
175°C		
145	30	-1
140	5	4 - (2 + 1)
85	55	(3 + 4) - (1 + 2)
55	30	3 - (1 + 2)
25	30	3 - 2

Note: Duplicated temperatures are omitted. The interval  $\Delta T$  and streams in the intervals are included as they are needed for Table 3.6.

Table 3.6. Problem table

Interval	Interval temp. °C	$\Delta T_n$ °C	$\Sigma CP_c - \Sigma CP_h^*$ kW/°C	$\Delta H$ kW	Surplus or Deficit
	175				
1	145	30	-3.0	-90	s
2	140	5	0.5	2.5	d
3	85	55	2.5	137.5	d
4	55	30	-2.0	-60	s
5	25	30	1.0	30	d

\*Note: The streams in each interval are given in Table 3.5.

5. "Cascade" the heat surplus from one interval to the next down the column of interval temperatures; Figure 3.23a.

Cascading the heat from one interval to the next implies that the temperature difference is such that the heat can be transferred between the hot and cold streams. The presence

Interval temp.				
	0 kW		50 kW	
175°C	-90 kW		-90 kW	
145°C	2.5 kW	90 kW	2.5 kW	140 kW
140°C	137.5 kW	87.5 kW	137.5 kW	135.5 kW
85°C	-60 kW	-50 kW	-60 kW	0.0 kW
55°C	30 kW	10 kW	30 kW	60 kW
25°C		-20 kW		30 kW
	(a)		(b)	

From (b) pinch occurs at interval temperature = 85°C.

Figure 3.23. Heat cascade

of a negative value in the column indicates that the temperature gradient is in the wrong direction and that the exchange is not thermodynamically possible.

This difficulty can be overcome if heat is introduced into the top of the cascade:

6. Introduce just enough heat to the top of the cascade to eliminate all the negative values; see Figure 3.23*b*.

Comparing the composite curve, Figure 3.22, with Figure 3.23*b* shows that the heat introduced to the cascade is the minimum hot utility requirement and the heat removed at the bottom is the minimum cold utility required. The pinch occurs in Figure 3.23*b* where the heat flow in the cascade is zero. This is as would be expected from the rule that for minimum utility requirements no heat flows across the pinch. In Figure 3.23*b* the pinch temperatures are 80 and 90°C, as was found using the composite stream curves.

It is not necessary to draw up a separate cascade diagram. This was done in Figure 3.23 to illustrate the principle. The cascaded values can be added to the problem table as two additional columns; see example 3.16.

### Summary

For maximum heat recovery and minimum use of utilities:

1. Do not transfer heat across the pinch
2. Do not use hot utilities below the pinch
3. Do not use cold utilities above the pinch

### 3.17.3. The heat exchanger network

#### Grid representation

It is convenient to represent a heat exchanger network as a grid; see Figure 3.24. The process streams are drawn as horizontal lines, with the stream numbers shown in square boxes. Hot streams are drawn at the top of the grid, and flow from left to right. The cold streams are drawn at the bottom, and flow from right to left. The stream heat capacities  $CP$  are shown in a column at the end of the stream lines.

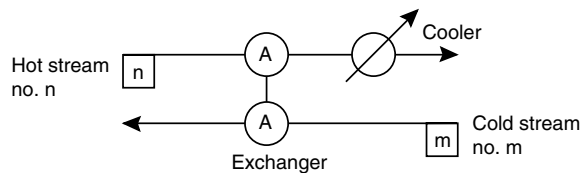


Figure 3.24. Grid representation

Heat exchangers are drawn as two circles connected by a vertical line. The circles connect the two streams between which heat is being exchanged; that is, the streams that would flow through the actual exchanger. Heater and coolers are drawn as a single circle, connected to the appropriate utility.

### Network design for maximum energy recovery

The analysis carried out in Figure 3.22, and Figure 3.23, has shown that the minimum utility requirements for the problem set out in Table 3.3 are 50 kW of the hot and 30 kW of the cold utility; and that the pinch occurs where the cold streams are at 80 and the hot 90°C.

The grid representation of the streams is shown in Figure 3.25. The vertical dotted lines represent the pinch and separate the grid into the regions above and below the pinch.

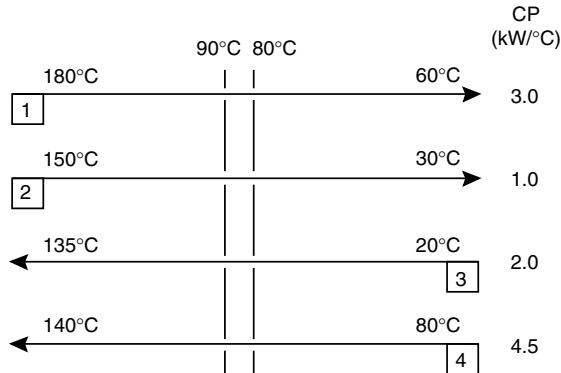


Figure 3.25. Grid for 4 stream problem

For maximum energy recovery (minimum utility consumption) the best performance is obtained if no cooling is used above the pinch. This means that the hot streams above the pinch should be brought to the pinch temperature solely by exchange with the cold streams. The network design is therefore started at the pinch; finding feasible matches between streams to fulfil this aim. In making a match adjacent to the pinch the heat capacity  $CP$  of the hot stream should be equal to or less than that of the cold stream. This is to ensure that the minimum temperature difference between the curves is maintained. The slope of a line on the temperature-enthalpy diagram is equal to the reciprocal of the heat capacity. So, above the pinch the lines will converge if  $CP_{hot}$  exceeds  $CP_{cold}$  and as the streams start with a separation at the pinch equal to  $\Delta T_{min}$ , the minimum temperature condition would be violated.

Below the pinch the procedure is the same; the aim being to bring the cold streams to the pinch temperature by exchange with the hot streams. For streams adjacent to the pinch the criterion for matching streams is that the heat capacity of the cold stream must be equal to or greater than the hot stream, to avoid breaking the minimum temperature difference condition.

### The network design above the pinch

$$CP_{hot} \leq CP_{cold}$$

1. Applying this condition at the pinch, stream 1 can be matched with stream 4, but not with 3.

Matching streams 1 and 4 and transferring the full amount of heat required to bring stream 1 to the pinch temperature gives:

$$\Delta H_{\text{ex}} = CP(T_s - T_{\text{pinch}})$$

$$\Delta H_{\text{ex}} = 3.0(180 - 90) = 270 \text{ kW}$$

This will also satisfy the heat load required to bring stream 4 to its target temperature:

$$\Delta H_{\text{ex}} = 4.5(140 - 80) = 270 \text{ kW}$$

2. Stream 2 can be matched with stream 3, whilst satisfying the heat capacity restriction. Transferring the full amount to bring stream 3 to the pinch temperature:

$$\Delta H_{\text{ex}} = 1.0(150 - 90) = 60 \text{ kW}$$

3. The heat required to bring stream 3 to its target temperature, from the pinch temperature, is:

$$\Delta H = 2.0(135 - 80) = 110 \text{ kW}$$

So a heater will have to be included to provide the remaining heat load:

$$\Delta H_{\text{hot}} = 110 - 60 = 50 \text{ kW}$$

This checks with the value given by the problem table, Figure 3.23*b*.

The proposed network design above the pinch is shown in Figure 3.26.

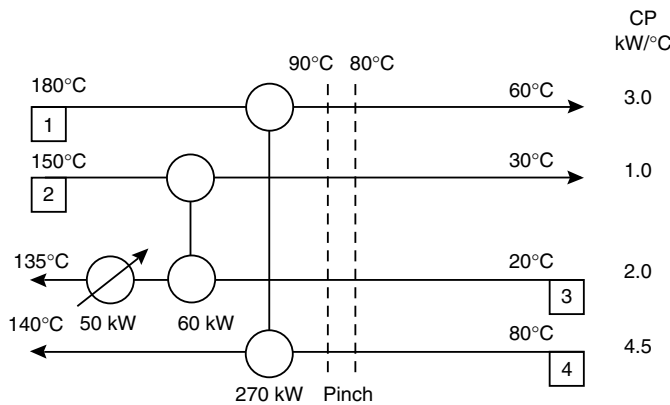


Figure 3.26. Network design above pinch

**Network design below the pinch**

$$CP_{\text{hot}} \geq CP_{\text{cold}}$$

4. Stream 4 is at the pinch temperature,  $T_s = 80^\circ\text{C}$ .

5. A match between stream 1 and 3 adjacent to the pinch will satisfy the heat capacity restriction but not one between streams 2 and 3. So 1 is matched with 3 transferring the full amount to bring stream 1 to its target temperature; transferring:

$$\Delta H_{\text{ex}} = 3.0(90 - 60) = 90 \text{ kW}$$



6. Stream 3 requires more heat to bring it to the pinch temperature; amount needed:

$$\Delta H = 2.0(80 - 20) - 90 = 30 \text{ kW}$$

This can be provided from stream 2, as the match will now be away from the pinch. The rise in temperature of stream 3 will be given by:

$$\Delta T = \Delta H / CP$$

So transferring 30 kW will raise the temperature from the source temperature to:

$$20 + 30/2.0 = 35^\circ\text{C}$$

and this gives a stream temperature difference on the outlet side of the exchanger of:

$$90 - 35 = 55^\circ\text{C}$$

So the minimum temperature difference condition,  $10^\circ\text{C}$ , will not be violated by this match.

7. Stream 2 will need further cooling to bring it to its target temperature, so a cooler must be included; cooling required.

$$\Delta H_{\text{cold}} = 1.0(90 - 30) - 30 = 30 \text{ kW}$$

Which is the amount of the cold utility predicted by the problem table.

The proposed network for maximum energy recovery is shown in Figure 3.27.

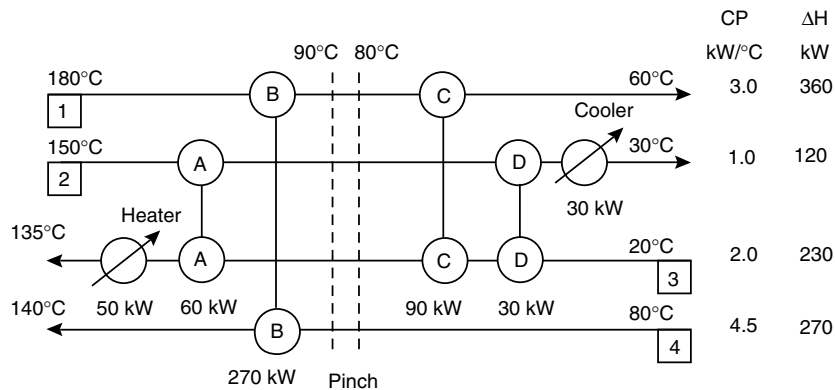


Figure 3.27. Proposed heat exchanger network  $\Delta T_{\min} = 10^\circ\text{C}$

### Stream splitting

If the heat capacities of streams are such that it is not possible to make a match at the pinch without violating the minimum temperature difference condition, then the heat capacity can be altered by splitting a stream. Dividing the stream will reduce the mass flow-rates in each leg and hence the heat capacities. This is illustrated in Example 3.16.

Guide rules for stream matching and splitting are given in the Institution of Chemical Engineers Guide, IChemE (1994).

## Summary

The heuristics (guide rules) for devising a network for maximum heat recovery are given below:

1. Divide the problem at the pinch.
2. Design away from the pinch.
3. Above the pinch match streams adjacent to the pinch, meeting the restriction:

$$CP_{\text{hot}} \leq CP_{\text{cold}}$$

4. Below the pinch match streams adjacent to the pinch, meeting the restriction:

$$CP_{\text{hot}} \geq CP_{\text{cold}}$$

5. If the stream matching criteria can not be satisfied split a stream.
6. Maximise the exchanger heat loads.
7. Supply external heating only above the pinch, and external cooling only below the pinch.

### 3.17.4. Minimum number of exchangers

The network shown in Figure 3.27 was designed to give the maximum heat recovery, and will therefore give the minimum consumption, and cost, of the hot and cold utilities.

This will not necessarily be the optimum design for the network. The optimum design will be that which gives the lowest total annual costs: taking into account the capital cost of the system, in addition to the utility and other operating costs. The number of exchangers in the network, and their size, will determine the capital cost.

In Figure 3.27 it is clear that there is scope for reducing the number of exchangers. Exchanger D can be deleted and the heat loads of the cooler and heater increased to bring streams 2 and 3 to their target temperatures. Heat would cross the pinch and the consumption of the utilities would be increased. Whether the revised network would be better, more economic, would depend on the relative cost of capital and utilities. For any network there will be an optimum design that gives the least annual cost: capital charges plus utility and other operating costs. The estimation of capital and operating costs are covered in Chapter 6.

To find the optimum design it will be necessary to cost a number of alternative designs, seeking a compromise between the capital costs, determined by the number and size of the exchangers, and the utility costs, determined by the heat recovery achieved.

For simple networks Holmann (1971) has shown that the minimum number of exchangers is given by:

$$Z_{\min} = N' - 1 \quad (3.41)$$

where  $Z_{\min}$  = minimum number of exchangers needed, including heaters and coolers

$N'$  = the number of streams, including the utilities

For complex networks a more general expression is needed to determine the minimum number of exchangers:

$$Z_{\min} = N' + L' - S \quad (3.42)$$

where  $L'$  = the number of internal loops present in the network

$S$  = the number of independent branches (subsets) that exist in the network.

A loop exists where a close path can be traced through the network. There is a loop in the network shown in Figure 3.27. The loop is shown in Figure 3.28. The presence of a loop indicates that there is scope for reducing the number of exchangers.

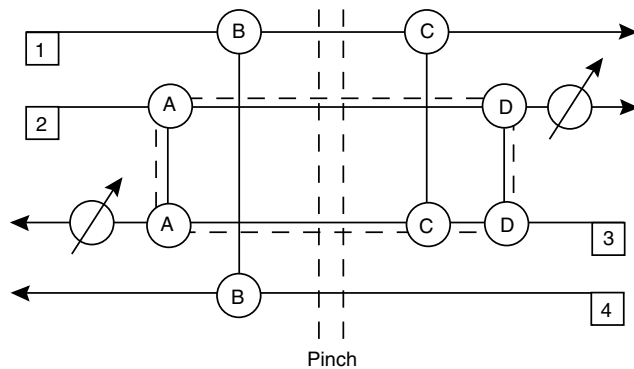


Figure 3.28. Loop in network

For a full discussion of equation 3.42 and its applications see Linnhoff *et al.* (1979), and IChemE (1994).

In summary, to seek the optimum design for a network:

1. Start with the design for maximum heat recovery. The number of exchangers needed will be equal to or less than the number for maximum energy recovery.
2. Identify loops that cross the pinch. The design for maximum heat recovery will usually contain loops.
3. Starting with the loop with the least heat load, break the loops by adding or subtracting heat.
4. Check that the specified minimum temperature difference  $\Delta T_{\min}$  has not been violated, and revise the design as necessary to restore the  $\Delta T_{\min}$ .
5. Estimate the capital and operating costs, and the total annual cost.
6. Repeat the loop breaking and network revision to find the lowest cost design.
7. Consider the safety, operability and maintenance aspects of the proposed design.

### Importance of the minimum temperature difference

In a heat exchanger, the heat-transfer area required to transfer a specified heat load is inversely proportional to the temperature difference between the streams; see Chapter 12.

This means that the value chosen for  $\Delta T_{\min}$  will determine the size of the heat exchangers in a network. Reducing  $\Delta T_{\min}$  will increase the heat recovery, decreasing the utility consumption and cost, but at the expense of an increase in the exchanger size and capital cost.

For any network there will be a best value for the minimum temperature difference that will give the lowest total annual costs. The effect of changes in the specified  $\Delta T_{\min}$  need to be investigated when optimising a heat recovery system.

### 3.17.5. Threshold problems

Problems that show the characteristic of requiring only either a hot utility or a cold utility (but not both) over a range of minimum temperature differences, from zero up to a threshold value, are known as threshold problems. A threshold problem is illustrated in Figure 3.29.

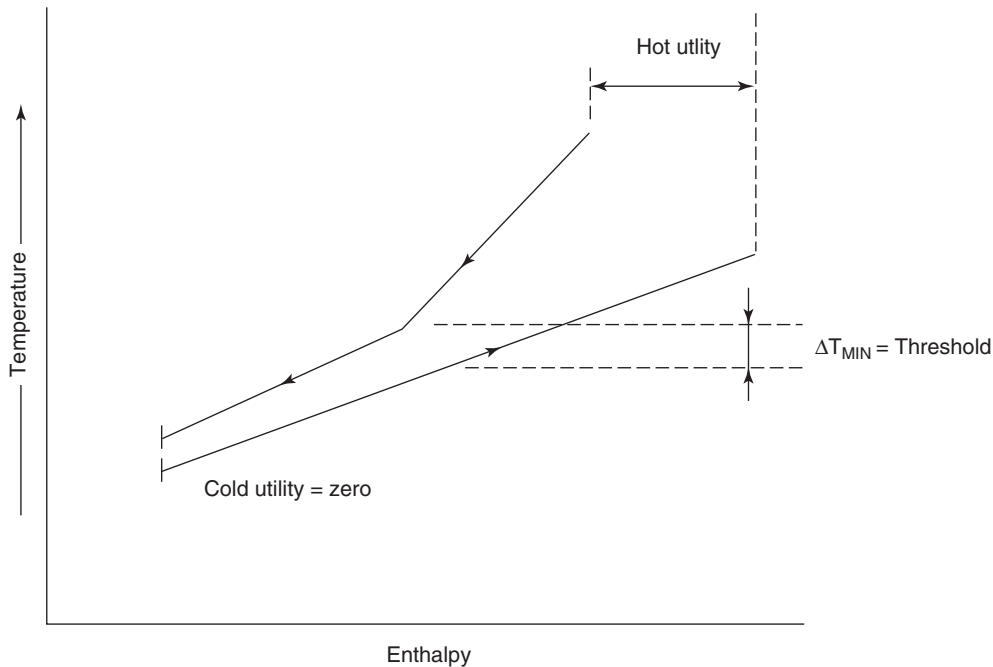


Figure 3.29. Threshold problem

To design the heat exchanger network for a threshold problem, it is normal to start at the most constrained point. The problem can often be treated as one half of a problem exhibiting a pinch.

Threshold problems are encountered in the process industries. A pinch can be introduced in such problems if multiple utilities are used, as in the recovery of heat to generate steam.

The procedures to follow in the design of threshold problems are discussed by Smith (1995) and IChemE (1994).

### 3.17.6. Multiple pinches and multiple utilities

The use of multiple utilities can lead to more than one pinch in a problem. In introducing multiple utilities the best strategy is to generate at the highest level and use at the lowest level. For a detailed discussion of this type of problem refer to Smith (1995) and IChemE (1994).

### 3.17.7. Process integration: integration of other process operations

The use of the pinch technology method in the design of heat exchanger networks has been outlined in Sections 3.17.1 to 3.17.6. The method can also be applied to the integration of other process units; such as, separation column, reactors, compressors and expanders, boilers and heat pumps. The wider applications of pinch technology are discussed in the Institution of Chemical Engineers Guide, IChemE (1994) and by Linnhoff *et al.* (1983), and Townsend and Linnhoff (1982), (1983), (1993).

Some guide rules for process integration:

1. Install combined heat and power (co-generation) systems across the pinch; see Chapter 14.
2. Install heat engines either above or below the pinch.
3. Install distillation columns above or below the pinch.
4. Install heat pumps across the pinch; see Section 3.16.7.

The techniques of process integration have been expanded for use in optimising mass transfer operations, and have been applied in waste reduction, water conservation, and pollution control, see Dunn and El-Halwagi (2003).

### Example 3.18

Determine the pinch temperatures and the minimum utility requirements for the streams set out in the table below, for a minimum temperature difference between the streams of 20°C. Devise a heat exchanger network to achieve the maximum energy recovery.

Stream number	Type	Heat capacity kW/°C	Source temp. °C	Target temp. °C	Heat load kW
1	hot	40.0	180	40	5600
2	hot	30.0	150	60	2700
3	cold	60.0	30	180	9000
4	cold	20.0	80	160	1600

### Solution

The construction of the problem table to find the minimum utility requirement and the pinch temperature is facilitated by using a spreadsheet. The calculations in each cell are repetitive and the formula can be copied from cell to cell using the cell copy commands.

The spreadsheet AS-EASY-AS (TRIOUS Inc) was used to develop the tables for this problem.

First calculate the interval temperatures, for  $\Delta T_{\min} = 20^\circ\text{C}$

hot streams  $T_{\text{int}} = T_{\text{act}} - 10^\circ\text{C}$

cold streams  $T_{\text{int}} = T_{\text{act}} + 10^\circ\text{C}$

Stream	Actual temp. °C		Interval temp. °C	
	Source	Target	Source	Target
1	180	40	170	30
2	150	60	140	50
3	30	180	40	190
4	80	160	90	(170)

Next rank the interval temperatures, ignoring any duplicated values. Show which streams occur in each interval to aid in the calculation of the combined stream heat capacities:

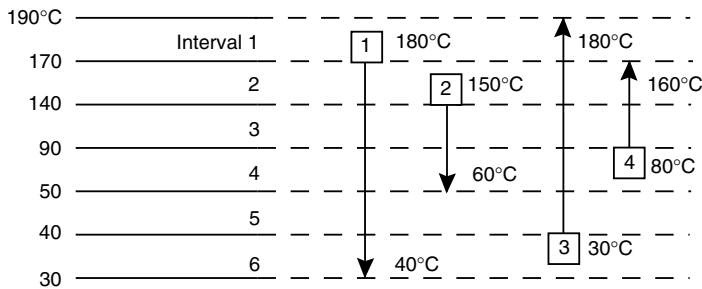


Figure 3.30. Intervals and streams

Now set out the problem table:

Interval	Interval temp. °C	$\Delta T$ °C	$\Sigma CP_c \times \Sigma CP_h$ kW/°C	$\Delta H$ kW	Cascade	
	190				0	2900
1	170	20	60.0	1200	-1200	1700
2	140	30	40.0	1200	-2400	500
3	90	50	10.0	500	-2900	0
4	50	40	-10.0	-400	-2500	400
5	40	10	20.0	200	-2700	200
6	30	10	-40.0	-400	-2300	600

In the last column 2900 kW of heat have been added to eliminate the negative values in the previous column.

So, the hot utility requirement is 2900 kW and the cold, the bottom value in the column, is 600 kW.

The pinch occurs where the heat transferred is zero, that is at interval number 3, 90°C.

So at the pinch hot streams will be at:

$$90 + 10 = 100^{\circ}\text{C}$$

and the cold at:

$$90 - 10 = 80^{\circ}\text{C}$$

To design the network for maximum energy recovery: start at the pinch and match streams following the rules on stream heat capacities for matches adjacent to the pinch. Where a match is made: transfer the maximum amount of heat.

The proposed network is shown in Figure 3.31.

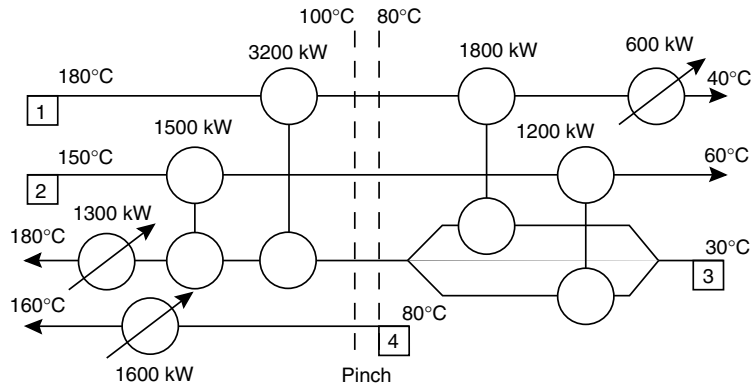


Figure 3.31. Network, example 3.17

The methodology followed in devising this network was:

### *Above pinch*

1.  $CP_{\text{hot}} \leq CP_{\text{cold}}$
2. Can match stream 1 and 2 with stream 3 but not with stream 4.
3. Check the heat available in bringing the hot streams to the pinch temperature.  
stream 1  $\Delta H = 40.0(180 - 100) = 3200 \text{ kW}$   
stream 2  $\Delta H = 30.0(150 - 100) = 1500 \text{ kW}$
4. Check the heat required to bring the cold streams from the pinch temperature to their target temperatures.  
stream 3  $\Delta H = 60.0(180 - 80) = 6000 \text{ kW}$   
stream 4  $\Delta H = 20.0(160 - 80) = 1600 \text{ kW}$
5. Match stream 1 with 3 and transfer 3200 kW, that satisfies (ticks off) stream 1.
6. Match stream 2 with 3 and transfer 1500 kW, that ticks off stream 2.
7. Include a heater on stream 3 to provide the balance of the heat required:

$$\Delta H_{\text{hot}} = 6000 - 4700 = 1300 \text{ kW}$$

8. Include a heater on stream 4 to provide heat load required, 1600 kW.

*Below pinch*

9.  $CP_{\text{hot}} \geq CP_{\text{cold}}$
10. Note that stream 4 starts at the pinch temperature so can not provide any cooling below the pinch.
11. Cannot match stream 1 or 2 with stream 3 at the pinch.
12. So, split stream 3 to reduce  $CP$ . An even split will allow both streams 1 and 2 to be matched with the split streams adjacent to the pinch, so try this:
13. Check the heat available from bringing the hot streams from the pinch temperature to their target temperatures.  
stream 1  $\Delta H = 40.0(100 - 40) = 2400 \text{ kW}$   
stream 2  $\Delta H = 30.0(100 - 60) = 1200 \text{ kW}$
14. Check the heat required to bring the cold streams from their source temperatures to the pinch temperature:  
stream 3  $\Delta H = 60.0(80 - 30) = 3000 \text{ kW}$   
stream 4 is at the pinch temperature.
15. Note that stream 1 can not be brought to its target temperature of  $40^\circ\text{C}$  by full interchange with stream 3 as the source temperature of stream 3 is  $30^\circ\text{C}$ , so  $\Delta T_{\text{min}}$  would be violated. So transfer 1800 kW to one leg of the split stream 3.
16. Check temperature at exit of this exchanger:

$$\text{Temp out} = 100 - \frac{1800}{40} = 55^\circ\text{C, satisfactory}$$

17. Provide cooler on stream 1 to bring it to its target temperature, cooling needed:

$$\Delta H_{\text{cold}} = 2400 - 1800 = 600 \text{ kW}$$

18. Transfer the full heat load from stream 2 to second leg of stream 3; this satisfies both streams.

Note that the heating and cooling loads, 2900 kW and 600 kW, respectively, match those predicted from the problem table.

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### 3.19. NOMENCLATURE

		Dimensions in $MLT\theta$
$a$	Constant in specific heat equation (equation 3.13)	$L^2T^{-2}\theta^{-1}$
$b$	Constant in specific heat equation (equation 3.13)	$L^2T^{-2}\theta^{-2}$
$CP$	Stream heat capacity	$ML^2T^{-2}\theta^{-1}$
$C_p$	Specific heat at constant pressure	$L^2T^{-2}\theta^{-1}$
$C_{pa}$	Specific heat component $a$	$L^2T^{-2}\theta^{-1}$
$C_{pb}$	Specific heat component $b$	$L^2T^{-2}\theta^{-1}$
$C_{pc}$	Specific heat component $c$	$L^2T^{-2}\theta^{-1}$
$C_{pm}$	Mean specific heat	$L^2T^{-2}\theta^{-1}$
$C_{p1}$	Specific heat first phase	$L^2T^{-2}\theta^{-1}$

$C_{p2}$	Specific heat second phase	$L^2T^{-2}\theta^{-1}$
$C_v$	Specific heat at constant volume	$L^2T^{-2}\theta^{-1}$
$C_p^o$	Ideal gas state specific heat	$L^2T^{-2}\theta^{-1}$
$c$	Constant in specific heat equation (equation 3.13)	$L^2T^{-2}\theta^{-3}$ or $L^2T^{-2}\theta^{-1/2}$
$\Sigma CP_c$	Sum of heat capacities of cold streams	$ML^2T^{-2}\theta^{-1}$
$\Sigma CP_h$	Sum of heat capacities of hot streams	$ML^2T^{-2}\theta^{-1}$
$E_e$	Efficiency, electric motors	—
$E_p$	Polytropic efficiency, compressors and turbines	—
$F$	Force	$MLT^{-2}$
$g$	Gravitational acceleration	$LT^{-2}$
$H$	Enthalpy	$ML^2T^{-2}$
$H_a$	Specific enthalpy of component $a$	$L^2T^{-2}$
$H_b$	Specific enthalpy of component $b$	$L^2T^{-2}$
$H_d$	Enthalpy top product stream (Example 3.1)	$ML^2T^{-3}$
$H_f$	Enthalpy feed stream (Example 3.1)	$ML^2T^{-3}$
$H_T$	Specific enthalpy at temperature $T$	$L^2T^{-2}$
$H_w$	Enthalpy bottom product stream (Example 3.1)	$ML^2T^{-3}$
$\Delta H$	Change in enthalpy	$ML^2T^{-2}$
$\Delta H_{\text{cold}}$	Heat transfer from cold utility	$ML^2T^{-3}$
$\Delta H_{\text{ex}}$	Heat transfer in exchanger	$ML^2T^{-3}$
$\Delta H_{\text{hot}}$	Heat transfer from hot utility	$ML^2T^{-3}$
$\Delta H_n$	Heat available in $n$ th interval	$ML^2T^{-3}$
$-\Delta H_{m,t}$	Heat of mixing at temperature $t$	$L^2T^{-2}$
$-\Delta H_{r,t}$	Heat of reaction at temperature $t$	$L^2T^{-2}$
$-\Delta H_c^o$	Standard heat of combustion	$L^2T^{-2}$
$\Delta H_f^o$	Standard enthalpy of formation	$L^2T^{-2}$
$-\Delta H_m^o$	Standard heat of mixing	$L^2T^{-2}$
$-\Delta H_r^o$	Standard heat of reaction	$L^2T^{-2}$
$L$	Number of auxiliary streams, heat exchanger networks	—
$L'$	Number of internal loops in network	—
$l$	Distance	$L$
$M$	Number of hot streams, heat-exchanger networks	—
$M$	Molecular mass (weight)	—
$m$	Polytropic temperature exponent	—
$m$	Mass	$M$
$m$	Mass flow-rate	$MT^{-1}$
$N$	Number of cold streams, heat-exchanger networks	—
$N'$	Number of streams	—
$n$	Expansion or compression index (equation 3.30)	—
$P$	Pressure	$ML^{-1}T^{-2}$
$P_i$	Inter-stage pressure	$ML^{-1}T^{-2}$
$P_r$	Reduced pressure	—
$P_1$	Initial pressure	$ML^{-1}T^{-2}$
$P_2$	Final pressure	$ML^{-1}T^{-2}$
$Q$	Heat transferred across system boundary	$ML^2T^{-2}$ or $ML^2T^{-3}$
$Q_b$	Reboiler heat load (Example 3.1)	$ML^2T^{-3}$
$Q_c$	Condenser heat load (Example 3.1)	$ML^2T^{-3}$
$Q_p$	Heat added (or subtracted) from a system	$ML^2T^{-2}$ or $ML^2T^{-3}$
$Q_r$	Heat from reaction	$ML^2T^{-2}$ or $ML^2T^{-3}$
$Q_s$	Heat generated in the system	$ML^2T^{-2}$ or $ML^2T^{-3}$
$R$	Universal gas constant	$L^2T^{-2}\theta^{-1}$
$S$	Number of independent branches	—
$S_{c,j}$	Cold streams, heat-exchanger networks	—
$S_{hi}$	Hot streams, heat-exchanger networks	—
$S_{uk}$	Auxiliary streams, heat-exchanger networks	—
$T$	Temperature, absolute	$\theta$
$T_{\text{act}}$	Actual stream temperature	$\theta$

$T_d$	Datum temperature for enthalpy calculations	$\theta$
$T_{\text{int}}$	Interval temperature	$\theta$
$T_n$	Temperature in nth interval	$\theta$
$T_p$	Phase-transition temperature	$\theta$
$T_r$	Reduced temperature	—
$T_s$	Source temperature	$\theta$
$T_t$	Target temperature	$\theta$
$\Delta T_{\text{min}}$	Minimum temperature difference in heat exchanger	$\theta$
$\Delta T_n$	Internal temperature difference	$\theta$
$t$	Temperature, relative scale	$\theta$
$t$	Time	<b>T</b>
$t_r$	Reference temperature, mean specific heat	$\theta$
$t_f$	Inlet-stream temperatures, heat-exchanger networks	$\theta$
$t_o$	Outlet-stream temperatures, heat-exchanger networks	$\theta$
$U$	Internal energy per unit mass	$\text{L}^2\text{T}^{-2}$
$u$	Velocity	$\text{LT}^{-1}$
$V_1$	Initial volume	$\text{L}^3$
$V_2$	Final volume	$\text{L}^3$
$v$	Volume per unit mass	$\text{M}^{-1}\text{L}^3$
$X$	Compressibility function defined by equation 3.33	—
$x$	Distance	<b>L</b>
$x_a$	Mol fraction component $a$ in a mixture	—
$x_b$	Mol fraction component $b$ in a mixture	—
$x_c$	Mol fraction component $c$ in a mixture	—
$Y$	Compressibility function defined by equation 3.34	—
$W$	Work per unit mass	$\text{L}^2\text{T}^{-2}$
$W_i$	Heat capacity of streams in a heat-exchanger network	$\text{ML}^2\text{T}^{-3}\theta^{-1}$
$Z$	Compressibility factor	—
$z$	Height above datum	<b>L</b>
$Z_{\text{min}}$	Minimum number of heat exchangers in network	—

### 3.20. PROBLEMS

- A liquid stream leaves a reactor at a pressure of 100 bar. If the pressure is reduced to 3 bar in a turbine, estimate the maximum theoretical power that could be obtained from a flow-rate of 1000 kg/h. The density of the liquid is 850 kg/m<sup>3</sup>.
- Calculate the specific enthalpy of water at a pressure of 1 bar and temperature of 200°C. Check your value using steam tables. The specific heat capacity of water can be calculated from the equation:  
 $C_p = 4.2 - 2 \times 10^{-3}t$ ; where  $t$  is in °C and  $C_p$  in kJ/kg.  
 Take the other data required from Appendix C.
- A gas produced as a by-product from the carbonisation of coal has the following composition, mol per cent: carbon dioxide 4, carbon monoxide 15, hydrogen 50, methane 12, ethane 2, ethylene 4, benzene 2, balance nitrogen. Using the data given in Appendix C, calculate the gross and net calorific values of the gas. Give your answer in MJ/m<sup>3</sup>, at standard temperature and pressure.
- In the manufacture of aniline, liquid nitrobenzene at 20°C is fed to a vaporiser where it is vaporised in a stream of hydrogen. The hydrogen stream is at 30°C, and the vaporiser operates at 20 bar. For feed-rates of 2500 kg/h nitrobenzene and 366 kg/h hydrogen, estimate the heat input required. The nitrobenzene vapour is not superheated.

- 3.5.** Aniline is produced by the hydrogenation of nitrobenzene. The reaction takes place in a fluidised bed reactor operating at 270 °C and 20 bar. The excess heat of reaction is removed by a heat transfer fluid passing through tubes in the fluidised bed. Nitrobenzene vapour and hydrogen enter the reactor at a temperature of 260 °C. A typical reactor off-gas composition, mol per cent, is: aniline 10.73, cyclo-hexylamine 0.11, water 21.68, nitrobenzene 0.45, hydrogen 63.67, inerts (take as nitrogen) 3.66. Estimate the heat removed by the heat transfer fluid, for a feed-rate of nitrobenzene to the reactor of 2500 kg/h.  
The specific heat capacity of nitrobenzene can be estimate using the methods given in Chapter 8. Take the other data required from Appendix C.
- 3.6.** Hydrogen chloride is produced by burning chlorine with an excess of hydrogen. The reaction is highly exothermic and reaches equilibrium very rapidly. The equilibrium mixture contains approximately 4 per cent free chlorine but this is rapidly combined with the excess hydrogen as the mixture is cooled. Below 200 °C the conversion of chlorine is essentially complete.  
The burner is fitted with a cooling jacket, which cools the exit gases to 200 °C. The gases are further cooled, to 50 °C, in an external heat exchanger.  
For a production rate of 10,000 tonnes per year of hydrogen chloride, calculate the heat removed by the burner jacket and the heat removed in the external cooler. Take the excess hydrogen as 1 per cent over stoichiometric. The hydrogen supply contains 5 per cent inerts (take as nitrogen) and is fed to the burner at 25 °C. The chlorine is essentially pure and is fed to the burner as a saturated vapour. The burner operates at 1.5 bar.
- 3.7.** A supply of nitrogen is required as an inert gas for blanketing and purging vessels. After generation, the nitrogen is compressed and stored in a bank of cylinders, at a pressure of 5 barg. The inlet pressure to the compressor is 0.5 barg, and temperature 20 °C. Calculate the maximum power required to compress 100 m<sup>3</sup>/h. A single-stage reciprocating compressor will be used.
- 3.8.** Hydrogen chloride gas, produced by burning chlorine with hydrogen, is required at a supply pressure of 600 kN/m<sup>2</sup>, gauge. The pressure can be achieved by either operating the burner under pressure or by compressing the hydrogen chloride gas. For a production rate of hydrogen chloride of 10,000 kg/h, compare the power requirement of compressing the hydrogen supply to the burner, with that to compress the product hydrogen chloride. The chlorine feed will be supplied at the required pressure from a vaporiser. Both the hydrogen and chlorine feeds are essentially pure. Hydrogen will be supplied to the burner one percent excess of over the stoichiometric requirement.  
A two-stage centrifugal compressor will be used for both duties. Take the polytropic efficiency for both compressors as 70 per cent. The hydrogen supply pressure is 120 kN/m<sup>2</sup> and the temperature 25 °C. The hydrogen chloride is cooled to 50 °C after leaving the burner. Assume that the compressor intercooler cools the gas to 50 °C, for both duties.  
Which process would you select and why?

- 3.9.** Estimate the work required to compress ethylene from 32 MPa to 250 MPa in a two-stage reciprocating compressor where the gas is initially at 30 °C and leaves the intercooler at 30 °C. See Example 3.13.
- 3.10.** Determine the pinch temperature and the minimum utility requirements for the process set out below. Take the minimum approach temperature as 15 °C. Devise a heat exchanger network to achieve maximum energy recovery.

Stream number	Type	Heat capacity kW/°C	Source Temp. °C	Target Temp. °C
1	hot	13.5	180	80
2	hot	27.0	135	45
3	cold	53.5	60	100
4	cold	23.5	35	120

- 3.11.** Determine the pinch temperature and the minimum utility requirements for the process set out below. Take the minimum approach temperature as 15 °C. Devise a heat exchanger network to achieve maximum energy recovery.

Stream number	Type	Heat capacity kW/°C	Source Temp. °C	Target Temp. °C
1	hot	10.0	200	80
2	hot	20.0	155	50
3	hot	40.0	90	35
4	cold	30.0	60	100
5	cold	8.0	35	90

- 3.12.** To produce a high purity product two distillation columns are operated in series. The overhead stream from the first column is the feed to the second column. The overhead from the second column is the purified product. Both columns are conventional distillation columns fitted with reboilers and total condensers. The bottom products are passed to other processing units, which do not form part of this problem. The feed to the first column passes through a preheater. The condensate from the second column is passed through a product cooler. The duty for each stream is summarised below:

No.	Stream	Type	Source temp. °C.	Target temp. °C	Duty, kW
1	Feed preheater	cold	20	50	900
2	First condenser	hot	70	60	1350
3	Second condenser	hot	65	55	1100
4	First reboiler	cold	85	87	1400
5	Second reboiler	cold	75	77	900
6	Product cooler	hot	55	25	30

Find the minimum utility requirements for this process, for a minimum approach temperature of 10 °C.

Note: the stream heat capacity is given by dividing the exchanger duty by the temperature change.

## CHAPTER 4

# *Flow-sheeting*

### 4.1. INTRODUCTION

This chapter covers the preparation and presentation of the process flow-sheet. The flow-sheet is the key document in process design. It shows the arrangement of the equipment selected to carry out the process; the stream connections; stream flow-rates and compositions; and the operating conditions. It is a diagrammatic model of the process.

The flow-sheet will be used by the specialist design groups as the basis for their designs. This will include piping, instrumentation, equipment design and plant layout. It will also be used by operating personnel for the preparation of operating manuals and operator training. During plant start-up and subsequent operation, the flow-sheet forms a basis for comparison of operating performance with design.

The flow-sheet is drawn up from material balances made over the complete process and each individual unit. Energy balances are also made to determine the energy flows and the service requirements.

Manual flow-sheeting calculations can be tedious and time consuming when the process is large or complex, and computer-aided flow-sheeting programs are being increasingly used to facilitate this stage of process design. Their use enables the designer to consider different processes, and more alternative processing schemes, in his search for the best process and optimum process conditions. Some of the proprietary flow-sheeting programs available are discussed in this chapter. A simple linear flow-sheeting program is presented in detail and listed in the appendices.

In this chapter the calculation procedures used in flow-sheeting have for convenience been divided into manual calculation procedures and computer-aided procedures.

The next step in process design after the flow-sheet is the preparation of Piping and Instrumentation diagrams (abbreviated to P & I diagrams) often also called the Engineering Flow-sheet or Mechanical Flow-sheet. The P & I diagrams, as the name implies, show the engineering details of the process, and are based on the process flow-sheet. The preparation and presentation of P & I diagrams is discussed in Chapter 5. The abbreviation PFD (for Process Flow Diagram) is often used for process flow-sheets, and PID for Piping and Instrumentation Diagrams.

### 4.2. FLOW-SHEET PRESENTATION

As the process flow-sheet is the definitive document on the process, the presentation must be clear, comprehensive, accurate and complete. The various types of flow-sheet are discussed below.

### 4.2.1. Block diagrams

A block diagram is the simplest form of presentation. Each block can represent a single piece of equipment or a complete stage in the process. Block diagrams were used to illustrate the examples in Chapters 2 and 3. They are useful for showing simple processes. With complex processes, their use is limited to showing the overall process, broken down into its principal stages; as in Example 2.13 (Vinyl Chloride). In that example each block represented the equipment for a complete reaction stage: the reactor, separators and distillation columns.

Block diagrams are useful for representing a process in a simplified form in reports and textbooks, but have only a limited use as engineering documents.

The stream flow-rates and compositions can be shown on the diagram adjacent to the stream lines, when only a small amount of information is to be shown, or tabulated separately.

The blocks can be of any shape, but it is usually convenient to use a mixture of squares and circles, drawn with a template.

### 4.2.2. Pictorial representation

On the detailed flow-sheets used for design and operation, the equipment is normally drawn in a stylised pictorial form. For tender documents or company brochures, actual scale drawings of the equipment are sometimes used, but it is more usual to use a simplified representation. The symbols given in British Standard, BS 1553 (1977) "Graphical Symbols for General Engineering" Part 1, "Piping Systems and Plant" are recommended; though most design offices use their own standard symbols. A selection of symbols from BS 1553 is given in Appendix A. The American National Standards Institute (ANSI) has also published a set of symbols for use on flow-sheets. Austin (1979) has compared the British Standard, ANSI, and some proprietary flow-sheet symbols.

In Europe, the German standards organisation has published a set of guide rules and symbols for flow-sheet presentation, DIN 28004 (1988). This is available in an English translation from the British Standards Institution.

### 4.2.3. Presentation of stream flow-rates

The data on the flow-rate of each individual component, on the total stream flow-rate, and the percentage composition, can be shown on the flow-sheet in various ways. The simplest method, suitable for simple processes with few equipment pieces, is to tabulate the data in blocks alongside the process stream lines, as shown in Figure 4.1. Only a limited amount of information can be shown in this way, and it is difficult to make neat alterations or to add additional data.

A better method for the presentation of data on flow-sheets is shown in Figure 4.2. In this method each stream line is numbered and the data tabulated at the bottom of the sheet. Alterations and additions can be easily made. This is the method generally used by professional design offices. A typical commercial flow-sheet is shown in Figure 4.3. Guide rules for the layout of this type of flow-sheet presentation are given in Section 4.2.5.

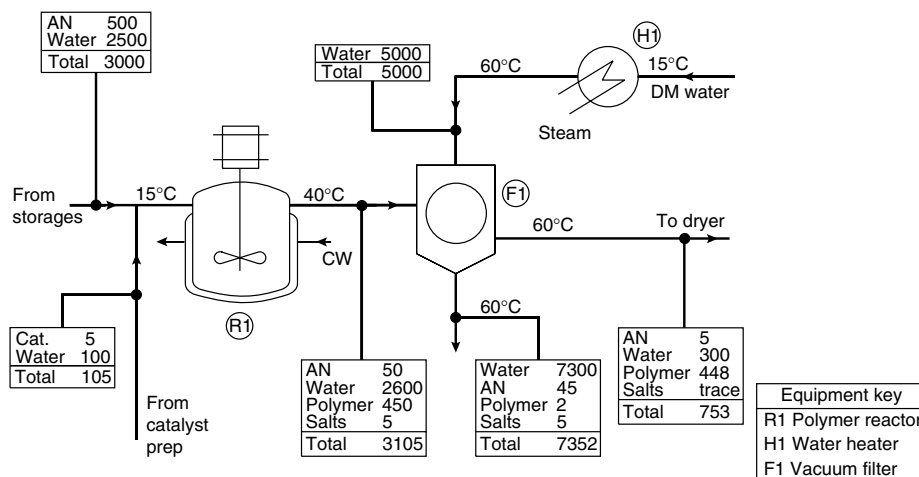


Figure 4.1. Flow-sheet: polymer production

#### 4.2.4. Information to be included

The amount of information shown on a flow-sheet will depend on the custom and practice of the particular design office. The list given below has therefore been divided into essential items and optional items. The essential items must always be shown, the optional items add to the usefulness of the flow-sheet but are not always included.

##### **Essential information**

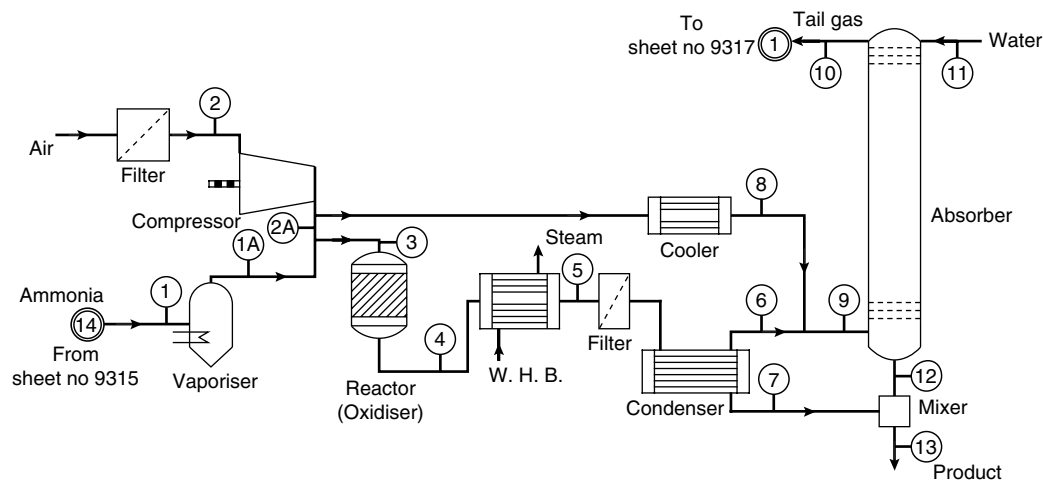
1. Stream composition, either:
  - (i) the flow-rate of each individual component, kg/h, which is preferred, or
  - (ii) the stream composition as a weight fraction.
2. Total stream flow-rate, kg/h.
3. Stream temperature, degrees Celsius preferred.
4. Nominal operating pressure (the required operating pressure).

##### **Optional information**

1. Molar percentages composition.
2. Physical property data, mean values for the stream, such as:
  - (i) density, kg/m<sup>3</sup>,
  - (ii) viscosity, mN s/m<sup>2</sup>.
3. Stream name, a brief, one or two-word, description of the nature of the stream, for example "ACETONE COLUMN BOTTOMS".
4. Stream enthalpy, kJ/h.

The stream physical properties are best estimated by the process engineer responsible for the flow-sheet. If they are then shown on the flow-sheet, they are available for use by the specialist design groups responsible for the subsequent detailed design. It is best that each group use the same estimates, rather than each decide its own values.





Flows kg/h Pressures nominal

Line no. Stream Component	1 Ammonia feed	1A Ammonia vapour	2 Filtered air	2A Oxidiser air	3 Oxidiser feed	4 Oxidiser outlet	5 W.H.B. outlet	6 Condenser gas	7 Condenser acid	8 Secondary air	9 Absorber feed	10 Tail(2) gas	11 Water feed	12 Absorber acid	13 Product acid	C & R Construction Inc
NH <sub>3</sub>	731.0	731.0	—	—	731.0	Nil	—	—	—	—	—	—	—	—	—	Nitric acid 60 per cent 100,000 t/y
O <sub>2</sub>	—	—	3036.9	2628.2	2628.2	935.7	(935.7) <sup>(1)</sup>	275.2	Trace	408.7	683.9	371.5	—	Trace	Trace	
N <sub>2</sub>	—	—	9990.8	8644.7	8644.7	8668.8	(1238.4) <sup>(1)</sup>	8668.8	Trace	1346.1	10,014.7	10,014.7	—	Trace	Trace	Sheet no. 9316
NO	—	—	—	—	—	1238.4	(1238.4) <sup>(1)</sup>	202.5	—	—	202.5	21.9	—	Trace	Trace	
NO <sub>2</sub>	—	—	—	—	—	—	Trace	(?) <sup>(1)</sup>	967.2	—	—	967.2	(Trace) <sup>(1)</sup>	—	Trace	2554.6 2146.0
HNO <sub>3</sub>	—	—	—	—	—	—	Nil	Nil	—	850.6	—	—	—	—	1704.0	
H <sub>2</sub> O	—	—	—	Trace	—	—	1161.0	1161.0	29.4	1010.1	—	29.4	26.3	1376.9	1136.0	2146.0
<b>Total</b>	<b>731.0</b>	<b>731.0</b>	<b>13,027.7</b>	<b>11,272.9</b>	<b>12,003.9</b>	<b>12,003.9</b>	<b>12,003.9</b>	<b>10,143.1</b>	<b>1860.7</b>	<b>1754.8</b>	<b>11,897.7</b>	<b>10,434.4</b>	<b>1376.9</b>	<b>2840.0</b>	<b>4700.6</b>	
Press bar	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1	Dwg by Date Checked 25/7/1980
Temp. °C	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43	

Figure 4.2. Flow-sheet: simplified nitric acid process (Example 4.2)  
(1) See example

C & R Construction Inc.

Title : Nitric Acid 60 per cent

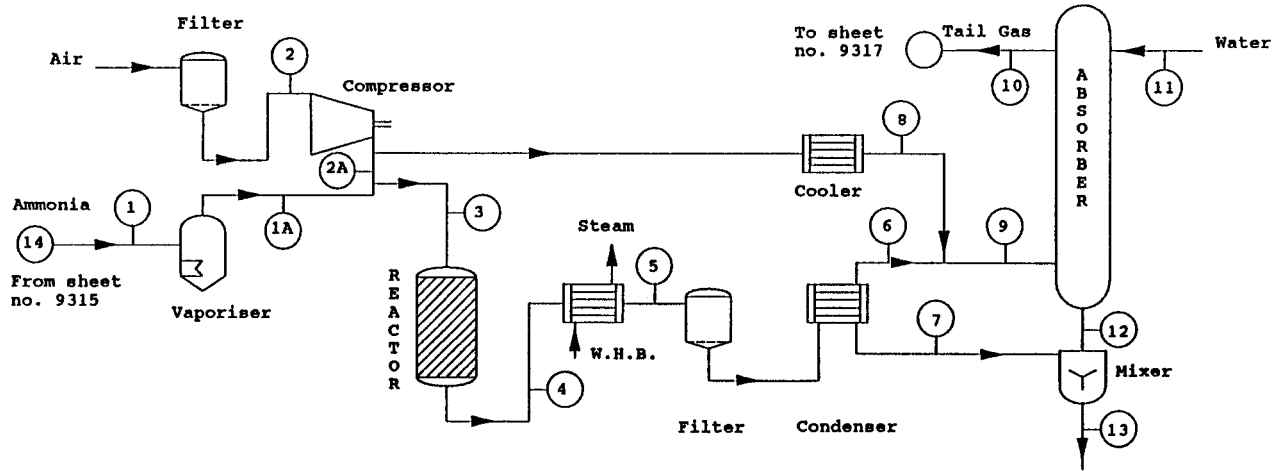
Dwg by : GRM

DATE :

Client : BOP Chemicals SILGO

Chk by : RKS

14/12/1992



Flows (kg/h) Pressures nominal

Line No.	1	1A	2	2A	3	4	5	6	7	8	9	10	11	12	13
Stream	Ammonia Feed	Ammonia Vapour	Filtered Air	Oxidiser Air	Oxidiser Feed	Oxidiser Outlet	W.H.B. Outlet	Condenser Gas	Condenser Acid	Condenser Air	Absorber Feed	Tail (2) Gas	Water Feed	Absorber Acid	Product Acid
Component															
NH3	731.0	731.0	--	--	731.0	NIL	--	--	--	--	--	--	--	--	--
O2	--	--	3036.9	2628.2	2628.2	935.7	935.7	275.2	TRACE	408.7	683.9	371.5	--	TRACE	TRACE
N2	--	--	9990.8	8644.7	8644.7	8668.8	8668.8	8668.8	TRACE	1346.1	10014.7	10014.7	--	TRACE	TRACE
NO	--	--	--	--	--	1238.4	1238.4	202.5	--	--	202.5	21.9	--	TRACE	TRACE
NO2	--	--	--	--	--	TRACE	(?)	967.2	--	--	967.2	TRACE	--	TRACE	TRACE
HN03	--	--	--	--	--	NIL	NIL	--	850.6	--	--	--	--	1704.0	2554.6
H2O	--	--	TRACE	TRACE	--	1161.0	1161.0	29.4	1010.1	--	29.4	26.3	1376.9	1136.0	2146.0
Total	731.0	731.0	13027.7	11272.9	12003.9	12003.9	12003.9	10143.1	1860.7	1754.8	11897.7	10434.4	1376.9	2840.0	4700.6
Press (Bar)	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1
Temp (°C)	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43

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Figure 4.2a. Flow-sheet drawn using FLOSHEET



### 4.2.5. Layout

The sequence of the main equipment items shown symbolically on the flow-sheet follows that of the proposed plant layout. Some licence must be exercised in the placing of ancillary items, such as heat exchangers and pumps, or the layout will be too congested. But the aim should be to show the flow of material from stage to stage as it will occur, and to give a general impression of the layout of the actual process plant.

The equipment should be drawn approximately to scale. Again, some licence is allowed for the sake of clarity, but the principal equipment items should be drawn roughly in the correct proportion. Ancillary items can be drawn out of proportion. For a complex process, with many process units, several sheets may be needed, and the continuation of the process streams from one sheet to another must be clearly shown. One method of indicating a line continuation is shown in Figure 4.2; those lines which are continued over to another are indicated by a double concentric circle round the line number and the continuation sheet number written below.

The table of stream flows and other data can be placed above or below the equipment layout. Normal practice is to place it below. The components should be listed down the left-hand side of the table, as in Figure 4.2. For a long table it is good practice to repeat the list at the right-hand side, so the components can be traced across from either side.

The stream line numbers should follow consecutively from left to right of the layout, as far as is practicable; so that when reading the flow-sheet it is easy to locate a particular line and the associated column containing the data.

All the process stream lines shown on the flow-sheet should be numbered and the data for the stream given. There is always a temptation to leave out the data on a process stream if it is clearly just formed by the addition of two other streams, as at a junction, or if the composition is unchanged when flowing through a process unit, such as a heat exchanger; this should be avoided. What may be clear to the process designer is not necessarily clear to the others who will use the flow-sheet. Complete, unambiguous information on all streams should be given, even if this involves some repetition. The purpose of the flow-sheet is to show the function of each process unit; even to show when it has no function.

### 4.2.6. Precision of data

The total stream and individual component flows do not normally need to be shown to a high precision on the process flow-sheet; at most one decimal place is all that is usually justified by the accuracy of the flow-sheet calculations, and is sufficient. The flows should, however, balance to within the precision shown. If a stream or component flow is so small that it is less than the precision used for the larger flows, it can be shown to a greater number of places, if its accuracy justifies this and the information is required. Imprecise small flows are best shown as "TRACE". If the composition of a trace component is specified as a process constraint, as, say, for an effluent stream or product quality specification, it can be shown in parts per million, ppm.

A trace quantity should not be shown as zero, or the space in the tabulation left blank, unless the process designer *is sure* that it has no significance. Trace quantities can be important. Only a trace of an impurity is needed to poison a catalyst, and trace quantities

can determine the selection of the materials of construction; see Chapter 7. If the space in the data table is left blank opposite a particular component the quantity may be assumed to be zero by the specialist design groups who take their information from the flow-sheet.

#### **4.2.7. Basis of the calculation**

It is good practice to show on the flow-sheet the basis used for the flow-sheet calculations. This would include: the operating hours per year; the reaction and physical yields; and the datum temperature used for energy balances. It is also helpful to include a list of the principal assumptions used in the calculations. This alerts the user to any limitations that may have to be placed on the flow-sheet information.

#### **4.2.8. Batch processes**

Flow-sheets drawn up for batch processes normally show the quantities required to produce one batch. If a batch process forms part of an otherwise continuous process, it can be shown on the same flow-sheet, providing a clear break is made when tabulating the data between the continuous and batch sections; the change from kg/h to kg/batch. A continuous process may include batch make-up of minor reagents, such as the catalyst for a polymerisation process.

#### **4.2.9. Services (utilities)**

To avoid cluttering up the flow-sheet, it is not normal practice to show the service headers and lines on the process flow-sheet. The service connections required on each piece of equipment should be shown and labelled. The service requirements for each piece of equipment can be tabulated on the flow-sheet.

#### **4.2.10. Equipment identification**

Each piece of equipment shown on the flow-sheet must be identified with a code number and name. The identification number (usually a letter and some digits) will normally be that assigned to a particular piece of equipment as part of the general project control procedures, and will be used to identify it in all the project documents.

If the flow-sheet is not part of the documentation for a project, then a simple, but consistent, identification code should be devised. The easiest code is to use an initial letter to identify the type of equipment, followed by digits to identify the particular piece. For example, H—heat exchangers, C—columns, R—reactors. The key to the code should be shown on the flow-sheet.

#### **4.2.11. Computer aided drafting**

Most design offices now use computer aided drafting programs for the preparation of flow-sheets and other process drawings. When used for drawing flow-sheets, and piping and instrumentation diagrams (see Chapter 5), standard symbols representing the process equipment, instruments and control systems are held in files and called up as required.

To illustrate the use of a commercial computer aided design program, Figure 4.2 has been redrawn using the program FLOSHEET and is shown as Figure 4.2a. FLOSHEET is a versatile flow-sheet drafting program. It is used by many chemical engineering departments in the UK; see Preece (1986) and Preece and Stephens (1989).

FLOSHEET is part of a suite of programs called PROCEDE which has been developed for the efficient handling of all the information needed in process design. It aims to cover the complete process environment, using graphical user interfaces to facilitate the transfer of information, Preece *et al.* (1991). The equipment specification sheets given in Appendix G are from the PROCEDE package.

### 4.3. MANUAL FLOW-SHEET CALCULATIONS

This section is a general discussion of the techniques used for the preparation of flow-sheets from manual calculations. The stream flows and compositions are calculated from material balances; combined with the design equations that arise from the process and equipment design constraints.

As discussed in Chapter 1, there will be two kinds of design constraints:

*External constraints:* not directly under the control of the designer, and which cannot normally be relaxed. Examples of this kind of constraint are:

- (i) Product specifications, possibly set by customer requirements.
- (ii) Major safety considerations, such as flammability limits.
- (iii) Effluent specifications, set by government agencies.

*Internal constraints:* determined by the nature of the process and the equipment functions. These would include:

- (i) The process stoichiometry, reactor conversions and yields.
- (ii) Chemical equilibria.
- (iii) Physical equilibria, involved in liquid-liquid and gas/vapour-liquid separations.
- (iv) Azeotropes and other fixed compositions.
- (v) Energy-balance constraints. Where the energy and material balance interact, as for example in flash distillation.
- (vi) Any general limitations on equipment design.

The flow-sheet is usually drawn up at an early stage in the development of the project. A preliminary flow-sheet will help clarify the designer's concept of the process; and serve as basis for discussions with other members of the design team.

The extent to which the flow-sheet can be drawn up before any work is done on the detailed design of the equipment will depend on the complexity of the process and the information available. If the design is largely a duplication of an existing process, though possibly for a different capacity, the equipment performance will be known and the stream flows and compositions can be readily calculated. For new processes, and for major modifications of existing processes, it will only be possible to calculate some of

the flows independently of the equipment design considerations; other stream flows and compositions will be dependent on the equipment design and performance. To draw up the flow-sheet the designer must use his judgement in deciding which flows can be calculated directly; which are only weakly dependent on the equipment design; and which are determined by the equipment design.

By weakly dependent is meant those streams associated with equipment whose performance can be assumed, or approximated, without introducing significant errors in the flow-sheet. The detailed design of these items can be carried out later, to match the performance then specified by the flow-sheet. These will be items which in the designer's estimation do not introduce any serious cost penalty if not designed for their optimum performance. For example, in a phase separator, such as a decanter, if equilibrium between the phases is assumed the outlet stream compositions can be often calculated directly, independent of the separator design. The separator would be designed later, to give sufficient residence time for the streams to approach the equilibrium condition assumed in the flow-sheet calculation.

Strong interaction will occur where the stream flows and compositions are principally determined by the equipment design and performance. For example, the optimum conversion in a reactor system with recycle of the unreacted reagents will be determined by the performance of the separation stage, and reactor material balance cannot be made without considering the design of the separation equipment. To determine the stream flows and compositions it would be necessary to set up a mathematical model of the reactor-separator system, including costing.

To handle the manual calculations arising from complex processes, with strong interactions between the material balance calculations and the equipment design, and where physical recycle streams are present, it will be necessary to sub-divide the process into manageable sub-systems. With judgement, the designer can isolate those systems with strong interactions, or recycle, and calculate the flows sequentially, from sub-system to sub-system, making approximations as and where required. Each sub-system can be considered separately, if necessary, and the calculations repeatedly revised till a satisfactory flow-sheet for the complete process is obtained. To attempt to model a complex process without subdivision and approximation would involve too many variables and design equations to be handled manually. Computer flow-sheeting programs should be used if available.

When sub-dividing the process and approximating equipment performance to produce a flow-sheet, the designer must appreciate that the resulting design for the complete process, as defined by the flow-sheet, will be an approximation to the optimum design. He must continually be aware of, and check, the effect of his approximations on the performance of the complete process.

#### **4.3.1. Basis for the flow-sheet calculations**

##### ***Time basis***

No plant will operate continuously without shut-down. Planned shut-down periods will be necessary for maintenance, inspection, equipment cleaning, and the renewal of catalysts

and column packing. The frequency of shut-downs, and the consequent loss of production time, will depend on the nature of the process. For most chemical and petrochemical processes the plant attainment will typically be between 90 to 95 per cent of the total hours in a year (8760). Unless the process is known to require longer shut-down periods, a value of 8000 hours per year can be used for flow-sheet preparation.

### **Scaling factor**

It is usually easiest to carry out the sequence of flow-sheet calculations in the same order as the process steps; starting with the raw-material feeds and progressing stage by stage, where possible, through the process to the final product flow. The required production rate will usually be specified in terms of the product, not the raw-material feeds, so it will be necessary to select an arbitrary basis for the calculations, say 100 kmol/h of the principal raw material. The actual flows required can then be calculated by multiplying each flow by a scaling factor determined from the actual production rate required.

$$\text{Scaling factor} = \frac{\text{mols product per hour specified}}{\text{mols product produced per 100 kmol of the principal raw material}}$$

## **4.3.2. Flow-sheet calculations on individual units**

Some examples of how design constraints can be used to determine stream flows and compositions are given below.

### **1. Reactors**

- (i) Reactor yield and conversion specified.

The reactor performance may be specified independently of the detailed design of the reactor. The conditions for the optimum, or near optimum, performance may be known from the operation of existing plant or from pilot plant studies.

For processes that are well established, estimates of the reactor performance can often be obtained from the general and patent literature; for example, the production of nitric and sulphuric acids.

If the yields and conversions are known, the stream flows and compositions can be calculated from a material balance; see Example 2.13.

- (ii) Chemical equilibrium.

With fast reactions, the reaction products can often be assumed to have reached equilibrium. The product compositions can then be calculated from the equilibrium data for the reaction, at the chosen reactor temperature and pressure; see Example 4.1.

### **2. Equilibrium stage**

In a separation or mixing unit, the anticipated equipment performance may be such that it is reasonable to consider the outlet streams as being in equilibrium; the approach to equilibrium being in practice close enough that no significant inaccuracy is introduced



by assuming that equilibrium is reached. The stream compositions can then be calculated from the phase equilibrium data for the components. This approximation can often be made for single-stage gas-liquid and liquid-liquid separators, such as quench towers, partial condensers and decanters. It is particularly useful if one component is essentially non-condensable and can be used as a tie substance (see Section 2.11). Some examples of the use of this process constraint are given in Examples 4.2 and 4.4.

### 3. Fixed stream compositions

If the composition (or flow-rate) of one stream is fixed by “internal” or “external” constraints, this may fix the composition and flows of other process streams. In Chapter 1, the relationship between the process variables, the design variables and design equations was discussed. If sufficient design variables are fixed by external constraints, or by the designer, then the other stream flows round a unit will be uniquely determined. For example, if the composition of one product stream from a distillation column is fixed by a product specification, or if an azeotrope is formed, then the other stream composition can be calculated directly from the feed compositions; see Section 2.10. The feed composition would be fixed by the outlet composition of the preceding unit.

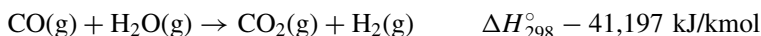
### 4. Combined heat and material balances

It is often possible to make a material balance round a unit independently of the heat balance. The process temperatures may be set by other process considerations, and the energy balance can then be made separately to determine the energy requirements to maintain the specified temperatures. For other processes the energy input will determine the process stream flows and compositions, and the two balances must be made simultaneously; for instance, in flash distillation or partial condensation; see also Example 4.1.

#### Example 4.1

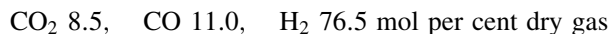
An example illustrating the calculation of stream composition from reaction equilibria, and also an example of a combined heat and material balance.

In the production of hydrogen by the steam reforming of hydrocarbons, the classic water-gas reaction is used to convert CO in the gases leaving the reforming furnace to hydrogen, in a shift converter.



In this example the exit gas stream composition from a converter will be determined for a given inlet gas composition and steam ratio; by assuming that in the outlet stream the gases reach chemical equilibrium. In practice the reaction is carried out over a catalyst, and the assumption that the outlet composition approaches the equilibrium composition is valid. Equilibrium constants for the reaction are readily available in the literature.

A typical gases composition obtained by steam reforming methane is:

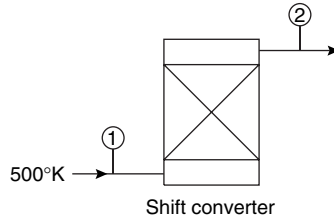


If this is fed to a shift converter at 500°K, with a steam ratio of 3 mol H<sub>2</sub>O to 1 mol CO, estimate the outlet composition and temperature.

**Solution**

Basis: 100 mol/h dry feed gas.

$$\text{H}_2\text{O in feed stream} = 3.0 \times 11.0 = 33 \text{ mol.}$$



Let fractional conversion of CO to H<sub>2</sub> be  $C$ . Then mols of CO reacted =  $11.0 \times C$ . From the stoichiometric equation and feed composition, the exit gas composition will be:

$$\text{CO} = 11.0(1 - C)$$

$$\text{CO}_2 = 8.5 + 11.0 \times C$$

$$\text{H}_2\text{O} = 33 - 11.0 \times C$$

$$\text{H}_2 = 76.5 + 11.0 \times C$$

At equilibrium

$$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}}$$

The temperature is high enough for the gases to be considered ideal, so the equilibrium constant is written in terms of partial pressure rather than fugacity, and the constant will not be affected by pressure. Mol fraction can be substituted for partial pressure. As the total mols in and out is constant, the equilibrium relationship can be written directly in mols of the components.

$$K_p = \frac{11(1 - C)(33 - 11C)}{(8.5 + 11C)(76.5 + 11C)}$$

Expanding and rearranging

$$(K_p 121 - 121)C^2 + (K_p 935 + 484)C + (K_p 650 - 363) = 0 \quad (1)$$

$K_p$  is a function of temperature.

For illustration, take  $T$  out =  $700^\circ\text{K}$ , at which  $K_p = 1.11 \times 10^{-1}$

$$-107.6C^2 + 587.8C - 290.85 = 0$$

$$C = 0.57$$

The reaction is exothermic and the operation can be taken as adiabatic, as no cooling is provided and the heat losses will be small.

The gas exit temperature will be a function of the conversion. The exit temperature must satisfy the adiabatic heat balance and the equilibrium relationship.

A heat balance was carried over a range of values for the conversion  $C$ , using the program Energy 1, Chapter 3. The value for which the program gives zero heat input or

output required (adiabatic) is the value that satisfies the conditions above. For a datum temperature of 25°C:

Data for energy-balance program

Component		Stream (mol)		$C_p^\circ$ (kJ/kmol)			
		1	2	a	b	c	d
1	CO <sub>2</sub>	8.5	8.5 + 11C	19.80	7.34 E-2	-5.6 E-5	17.15 E-9
2	CO	11.0	11(1 - C)	30.87	-1.29 E-2	27.9 E-6	-12.72 E-9
3	H <sub>2</sub> O	33.0	33 - 11C	32.24	19.24 E-4	10.56 E-6	-3.60 E-9
4	H <sub>2</sub>	76.5	76.5 + 11C	27.14	9.29 E-3	-13.81 E-6	7.65 E-9

Results

Outlet temp. (K)	$K_p$	C	Mols converted	Outlet composition, mol				Heat required Q
				CO	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub>	
550	$1.86 \times 10^{-2}$	0.88	9.68	1.32	18.18	23.32	86.18	-175,268
600	$3.69 \times 10^{-2}$	0.79	8.69	2.31	17.19	24.31	85.19	76,462
650	$6.61 \times 10^{-2}$	0.68	7.48	3.52	15.98	25.52	83.98	337,638

The values for the equilibrium constant  $K_p$  were taken from *Technical Data on Fuel*, Spiers.

The outlet temperature at which  $Q = 0$  was found by plotting temperature versus  $Q$  to be 580 K.

At 580 K,  $K_p = 2.82 \times 10^{-2}$ .

From equation (1)

$$-117.6C^2 + 510.4 + -344.7 = 0,$$

$$C = 0.83$$

### Outlet gas composition

$$\text{CO}_2 = 8.5 + 11 \times 0.83 = 17.6$$

$$\text{CO} = 11(1 - 0.83) = 1.9$$

$$\text{H}_2\text{O} = 33.0 - 11 \times 0.83 = 23.9$$

$$\text{H}_2 = 76.5 + 11 \times 0.83 = 85.6$$

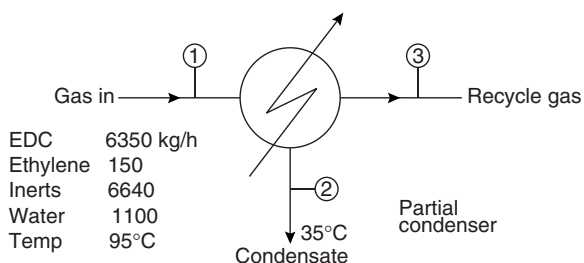
$$\underline{\hspace{1.5cm}} \\ 129.0 \text{ mol}$$

In this example the outlet exit gas composition has been calculated for an arbitrarily chosen steam: CO ratio of 3. In practice the calculation would be repeated for different steam ratios, and inlet temperatures, to optimise the design of the converter system. Two converters in series are normally used, with gas cooling between the stages. For large units a waste-heat boiler could be incorporated between the stages. The first stage conversion is normally around 80 per cent.

### Example 4.2

This example illustrates the use of phase equilibrium relationships (vapour-liquid) in material balance calculations.

In the production of dichloroethane (EDC) by oxyhydrochlorination of ethylene, the products from the reaction are quenched by direct contact with dilute HCl in a quench tower. The gaseous stream from this quench tower is fed to a condenser and the uncondensed vapours recycled to the reactor. A typical composition for this stream is shown in the diagram below; operating pressure 4 bar. Calculate the outlet stream compositions leaving the condenser.



The EDC flow includes some organic impurities and a trace of HCl. The inerts are mainly  $N_2$ ,  $CO$ ,  $O_2$  — non-condensable.

## Solution

In order to calculate the outlet stream composition it is reasonable, for a condenser, to assume that the gas and liquid streams are in equilibrium at the outlet liquid temperature of 35°C.

The vapour pressures of the pure liquids can be calculated from the Antoine equation (see Chapter 8):

At 35°C (308 K)	
EDC	0.16 bar
Ethylene	70.7
H <sub>2</sub> O	0.055

From the vapour pressures it can be seen that the EDC and water will be essentially totally condensed, and that the ethylene remains as vapour. Ethylene will, however, tend to be dissolved in the condensed EDC. As a first trial, assume all the ethylene stays in the gas phase.

Convert flows to mol/h.

	Mol wt.	kmol/h	
EDC	99	64	} 213.4
C <sub>2</sub> H <sub>4</sub>	28	5.4	
Inerts	32 (estimated)	208	
H <sub>2</sub> O	18	61	

Take the “non-condensables” (ethylene and inerts) as the tie substance. Treat gas phase as ideal, and condensed EDC-water as immiscible.

$$\begin{aligned} \text{Partial pressure of non-condensables} &= (\text{total pressure}) - (\text{vapour pressure of EDC} + \text{vapour pressure of water}) \\ &= 4 - 0.16 - 0.055 = \underline{\underline{3.79 \text{ bar}}} \end{aligned}$$

$$\begin{aligned} \text{Flow of EDC in vapour} &= \frac{\text{vapour press. EDC}}{\text{partial press. non-condensables}} \times \text{flow non-condensables} \\ &= \frac{0.16}{3.79} \times 213.4 = \underline{\underline{9 \text{ kmol/h}}} \end{aligned}$$

$$\begin{aligned} \text{Similarly, flow of H}_2\text{O in vapour} &= \frac{0.055}{3.79} \times 213.4 = \underline{\underline{3.1 \text{ kmol/h}}} \end{aligned}$$

So composition of gas streams is

	kmol/h	Per cent mol	kg/h
EDC	9	4.0	891
H <sub>2</sub> O	3.1	1.4	56
Inerts	208	92.3	6640
C <sub>2</sub> H <sub>4</sub>	5.4	2.3	150

### ***Check on dissolved ethylene***

$$\begin{aligned} \text{Partial pressure of ethylene} &= \text{total pressure} \times \text{mol fraction} \\ &= 4 \times \frac{2.3}{100} = 0.092 \text{ bar} \end{aligned}$$

By assuming EDC and C<sub>2</sub>H<sub>4</sub> form an ideal solution, the mol fraction of ethylene dissolved in the liquid can be estimated, from Raoult's Law (see Chapter 8).

$$y_A = \frac{x_A P_A^\circ}{P}$$

$y_A$  = gas phase mol fraction,

$x_A$  = liquid phase mol fraction,

$P_A^\circ$  = sat. vapour pressure,

$P$  = total pressure,

Substituting

$$\begin{aligned} \frac{2.3}{100} &= \frac{x_A 70.7}{4} \\ x_A &= 1.3 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \text{hence quantity of ethylene in liquid} &= \text{kmol EDC} \times x_A \\ &= (64 - 9) \times 1.3 \times 10^{-3} = 0.07 \text{ kmol/h} \end{aligned}$$

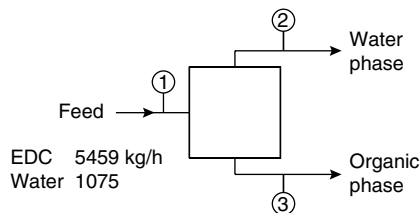
$$\begin{aligned} \text{so kmol ethylene in gas phase} &= 5.4 - 0.07 = \underline{\underline{5.33 \text{ kmol/h}}} \end{aligned}$$

This is little different from calculated value and shows that initial assumption that no ethylene was condensed or dissolved was reasonable; so report ethylene in liquid as “trace”.

Stream no.:	Material balance		Flows (kg/h)	
	1	2	3	
Title	Condenser feed	Condensate	Recycle gas	
EDC	6350	5459	891	
H <sub>2</sub> O	1100	1044	56	
Ethylene	150	Trace	150	
Inerts	6640	—	6640	
Total	14,240	6503	7737	
Temp. °C	95	35	35	
Pressure bar:	4	4	4	

### Example 4.3

This example illustrates the use of liquid-liquid phase equilibria in material balance calculations. The condensate stream from the condenser described in Example 4.2 is fed to a decanter to separate the condensed water and dichloroethane (EDC). Calculate the decanter outlet stream compositions.



### Solution

Assume outlet phases are in equilibrium.

The solubilities of the components at 20°C are:

EDC in water 0.86 kg/100 kg

Water in EDC 0.16 kg/100 kg

Note the water will contain a trace of HCl, but as data on the solubility of EDC in dilute HCl are not available, the solubility in water will be used.

As the concentrations of dissolved water and EDC are small, the best approach to this problem is by successive approximation; rather than by setting up and solving equations for the unknown concentrations.

As a first approximation take organic stream flow = EDC flow in.

$$\text{Then water in EDC} = \frac{0.16}{100} \times 5459 = 8.73 \text{ kg/h}$$

$$\text{So water flow out} = 1075 - 8.73 = 1066.3 \text{ kg/h}$$

$$\text{and EDC dissolved in the water stream} = \frac{1066.3}{100} \times 0.86 = 9.2 \text{ kg/h}$$

$$\text{so, revised organic stream flow} = 5459 - 9.2 = \underline{\underline{5449.8 \text{ kg/h}}}$$

$$\text{and quantity of water dissolved} = \frac{5449.8}{100} \times 0.16 = \underline{\underline{8.72 \text{ kg/h}}}$$

in the stream

Which is not significantly lower than the first approximation. So stream flows, kg/h, will be:

Stream no.	1	2	3
Title	Decanter feed	Organic phase	Aqueous phase
EDC	5459	5449.8	9.2
H <sub>2</sub> O	1075	8.7	1066.3
Total	6534	5458.5	1075.5

#### Example 4.4

This example illustrates the manual calculation of a material and energy balance for a process involving several processing units.

Draw up a preliminary flow-sheet for the manufacture of 20,000 t/y nitric acid (basis 100 per cent HNO<sub>3</sub>) from anhydrous ammonia, concentration of acid required 50 to 60 per cent.

The technology of nitric acid manufacture is well established and has been reported in several articles:

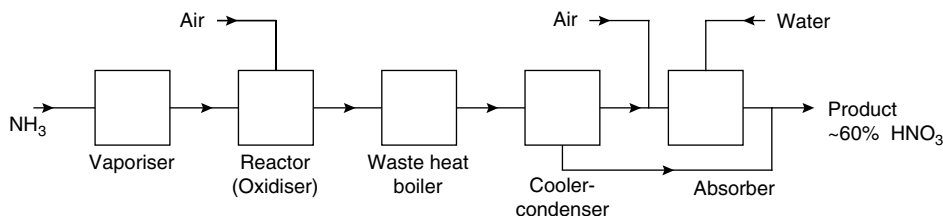
1. R. M. Stephenson: *Introduction to the Chemical Process Industries* (Reinhold, 1966).
2. C. H. Chilton: *The Manufacture of Nitric Acid by the Oxidation of Ammonia* (American Institute of Chemical Engineers).
3. S. Strelzoff: *Chem. Eng. NY* **63**(5), 170 (1956).
4. F. D. Miles: *Nitric Acid Manufacture and Uses* (Oxford University Press, 1961).

Three processes are used:

1. Oxidation and absorption at atmospheric pressure.
2. Oxidation and absorption at high pressure (approx. 8 atm).
3. Oxidation at atmospheric pressure and absorption at high pressure.

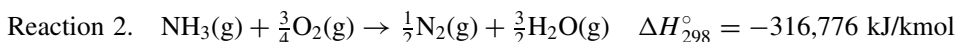
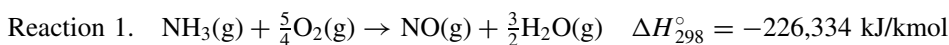
The relative merits of the three processes are discussed by Chilton (2), and Strelzoff (3).

For the purposes of this example the high-pressure process has been selected. A typical process is shown in the block diagram.

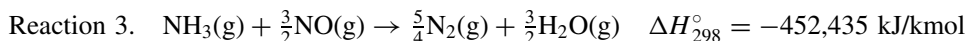


Schematic (block) diagram; production of nitric acid by oxidation of ammonia

The principal reactions in the reactor (oxidiser) are:



The nitric oxide formed can also react with ammonia:



The oxidation is carried out over layers of platinum-rhodium catalyst; and the reaction conditions are selected to favour reaction 1. Yields for the oxidation step are reported to be 95 to 96 per cent.

## Solution

### ***Basis of the flow-sheet calculations***

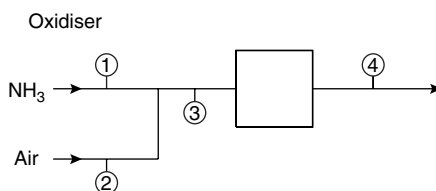
Typical values, taken from the literature cited:

1. 8000 operating hours per year.
2. Overall plant yield on ammonia 94 per cent.
3. Oxidiser (reactor) chemical yield 96 per cent.
4. Acid concentration produced 58 per cent w/w HNO<sub>3</sub>.
5. Tail gas composition 0.2 per cent v/v NO.

### ***Material balances***

Basis: 100 kmol NH<sub>3</sub> feed to reactor.

### ***Oxidiser***





From reaction 1, at 96 per cent yield,

$$\text{NO produced} = 100 \times \frac{96}{100} = 96 \text{ kmol}$$

$$\text{oxygen required} = 96 \times \frac{5}{4} = 120 \text{ kmol}$$

$$\text{water produced} = 96 \times \frac{3}{2} = 144 \text{ kmol}$$

The remaining 4 per cent ammonia reacts to produce nitrogen; production of 1 mol of  $\text{N}_2$  requires  $\frac{3}{2}$  mol of  $\text{O}_2$ , by either reaction 2 or 1 and 3 combined.

$$\text{nitrogen produced} = \frac{4}{2} = 2 \text{ kmol}$$

$$\text{oxygen required} = 2 \times \frac{3}{2} = 3 \text{ kmol}$$

All the oxygen involved in these reactions produces water,

$$\text{water produced} = 3 \times 2 = 6 \text{ kmol}$$

So, total oxygen required and water produced;

$$\text{water} = 144 + 6 = 150 \text{ kmol}$$

$$\text{oxygen (stoichiometric)} = 120 + 3 = 123 \text{ kmol}$$

Excess air is supplied to the oxidiser to keep the ammonia concentration below the explosive limit (see Chapter 9), reported to be 12 to 13 per cent (Chilton), and to provide oxygen for the oxidation of NO to  $\text{NO}_2$ .



The inlet concentration of ammonia will be taken as 11 per cent v/v.

$$\text{So, air supplied} = \frac{100}{11} \times 100 = 909 \text{ kmol}$$

Composition of air: 79 per cent  $\text{N}_2$ , 21 per cent  $\text{O}_2$ , v/v.

So, oxygen and nitrogen flows to oxidiser:

$$\text{oxygen} = 909 \times \frac{21}{100} = 191 \text{ kmol}$$

$$\text{nitrogen} = 909 \times \frac{79}{100} = 718 \text{ kmol}$$

And the oxygen unreacted (oxygen in the outlet stream) will be given by:

$$\text{oxygen unreacted} = 191 - 123 = 68 \text{ kmol}$$

The nitrogen in the outlet stream will be the sum of the nitrogen from the air and that produced from ammonia:

$$\text{nitrogen in outlet} = 718 + 2 = 720 \text{ kmol}$$

Summary, stream compositions:

	Feed (3)		Outlet (4)	
	kmol	kg	kmol	kg
NH <sub>3</sub>	100	1700	nil	
NO	nil		96	2880
H <sub>2</sub> O	trace		150	2700
O <sub>2</sub>	191	6112	68	2176
N <sub>2</sub>	718	20,104	720	20,016
Total		27,916		27,916

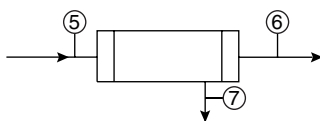
### Notes

- (1) The small amount of water in the inlet air is neglected.
- (2) Some NO<sub>2</sub> will be present in the outlet gases, but at the oxidiser temperature used, 1100 to 1200 K, the amount will be small, typically <1 per cent.
- (3) It is good practice always to check the balance across a unit by calculating the totals; total flow in must equal total flow out.

### Waste-heat boiler (WHB) and cooler-condenser

The temperature of the gases leaving the oxidiser is reduced in a waste-heat boiler and cooler-condenser. There will be no separation of material in the WHB but the composition will change, as NO is oxidised to NO<sub>2</sub> as the temperature falls. The amount oxidised will depend on the residence time and temperature (see Stephenson). The oxidation is essentially complete at the cooler-condenser outlet. The water in the gas condenses in the cooler-condenser to form dilute nitric acid, 40 to 50 per cent w/w.

### Balance on cooler-condenser



The inlet stream (5) will be taken as having the same composition as the reactor outlet stream (4).

Let the cooler-condenser outlet temperature be 40°C. The maximum temperature of the cooling water will be about 30°C, so this gives a 10°C approach temperature.

If the composition of the acid leaving the unit is taken as 45 per cent w/w (a typical value) the composition of the gas phase can be estimated by assuming that the gas and condensed liquid are in equilibrium at the outlet temperature.

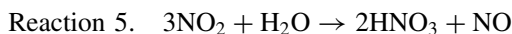
At 40°C the vapour pressure of water over 45 per cent HNO<sub>3</sub> is 29 mmHg (Perry's *Chemical Engineers Handbook*, 5th edn, pp. 3–65). Take the total pressure as 8 atm. The mol fraction of water in the outlet gas stream will be given by the ratio of the vapour pressure to the total pressure:

$$\text{mol fraction water} = \frac{29}{760 \times 8} = 4.77 \times 10^{-3}$$

As a first trial, assume that all the water in the inlet stream is condensed, then:

$$\text{water condensed} = 150 \text{ kmol} = 2700 \text{ kg}$$

NO<sub>2</sub> combines with this water to produce a 45 per cent solution:



For convenience, take as a subsidiary basis for this calculation 100 kmol of HNO<sub>3</sub> (100 per cent basis) in the condensate.

From reaction 5, the mols of water required to form 100 kmol HNO<sub>3</sub> will be:

$$50 \text{ kmol} = 900 \text{ kg}$$

$$\text{mass of 100 kmol HNO}_3 = 100 \times 63 = 6300 \text{ kg}$$

$$\text{water to dilute this to 45 per cent} = \frac{6300 \times 55}{45} = 7700 \text{ kg}$$

So, total water to form dilute acid = 900 + 7700 = 8600 kg.

Changing back to the original basis of 100 kmol NH<sub>3</sub> feed:

$$\begin{aligned} \text{HNO}_3 \text{ formed} &= 100 \times \frac{\text{Water condensed per 100 kmol NH}_3 \text{ feed}}{\text{Total water to form 45 per cent acid, per 100 kmol HNO}_3} \\ &= 100 \times \frac{2700}{8600} = 31.4 \text{ kmol} \end{aligned}$$

$$\text{NO}_2 \text{ consumed (from reaction 5)} = 31.4 \times \frac{3}{2} = 47.1 \text{ kmol}$$

$$\text{NO formed} = 31.4 \times \frac{1}{2} = 15.7 \text{ kmol}$$

$$\text{H}_2\text{O reacted} = 15.7 \text{ kmol}$$

Condensed water not reacted with NO<sub>2</sub> = 150 – 15.7 = 134.3 kmol.

The quantity of unoxidised NO in the gases leaving the cooler-condenser will depend on the residence time and the concentration of NO and NO<sub>2</sub> in the inlet stream. For simplicity in this preliminary balance the quantity of NO in the outlet gas will be taken as equal to the quantity formed from the absorption of NO<sub>2</sub> in the condensate to form nitric acid:

$$\text{NO in outlet gas} = 15.7 \text{ kmol}$$

The unreacted oxygen in the outlet stream can be calculated by making a balance over the unit on the nitric oxides, and on oxygen.

**Balance on oxides**

Total (NO + NO<sub>2</sub>) entering = NO in stream 4 = 96 kmol

Of this, 31.4 kmol leaves as nitric acid, so (NO + NO<sub>2</sub>) left in the gas stream = 96 - 31.4 = 64.6 kmol.

Of this, 15.7 kmol is assumed to be NO, so NO<sub>2</sub> in exit gas = 64.6 - 15.7 = 48.9 kmol.

**Balance on oxygen**

Let unreacted O<sub>2</sub> be  $x$  kmol. Then oxygen out of the unit will be given by:

$$\begin{aligned} & \left[ \frac{\text{NO}}{2} + \text{NO}_2 + x \right]_{\text{gas stream (6)}} + \left[ \frac{3}{2} \text{HNO}_3 + \frac{\text{H}_2\text{O}}{2} \right]_{\text{acid stream (7)}} \\ &= \left( \frac{15.7}{2} + 48.9 + x \right) + \left( \frac{3}{2} \times 31.4 + \frac{134.3}{2} \right) = (171 + x) \text{ kmol} \\ \text{Oxygen into the unit} &= \left[ \frac{\text{NO}}{2} + \text{O}_2 + \text{H}_2\text{O} \right]_{\text{stream (5)}} \\ &= \frac{96}{2} + 68 + \frac{150}{2} = 191 \text{ kmol} \end{aligned}$$

Equating O<sub>2</sub> in and out:

$$\text{unreacted O}_2, x, = 191 - 171 = 20.0 \text{ kmol}$$

As a first trial, all the water vapour was assumed to condense; this assumption will now be checked.

The quantity of water in the gas stream will be given by:

$$\text{mol fraction} \times \text{total flow.}$$

The total flow of gas (neglecting water) = 804.6 kmol, and the mol fraction of water was estimated to be  $4.77 \times 10^{-3}$ .

$$\text{So, water vapour} = 4.77 \times 10^{-3} \times 804.6 = 3.8 \text{ kmol}$$

And, mols of water condensed = 134.3 - 3.8 = 130.5 kmol.

The calculations could be repeated using this adjusted value for the quantity of water condensed, to get a better approximation, but the change in the acid, nitric oxides, oxygen and water flows will be small. So, the only change that will be made to the original estimates will be to reduce the quantity of condensed water by that estimated to be in the gas stream:

$$\text{Water in stream (6)} \ 3.8 \text{ kmol} = 68.4 \text{ kg}$$

So, water in stream (7) = 134.3 - 3.8 = 130.5 kmol = 2349 kg.

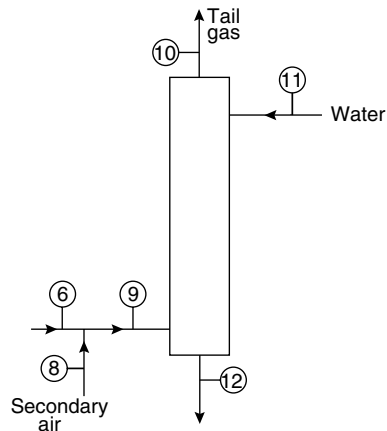
Summary, stream compositions:

	Gas (6)		Acid (7)	
	kmol	kg	kmol	kg
NO	15.7	471.0	Trace	
NO <sub>2</sub>	48.9	2249.4	Trace	
O <sub>2</sub>	20.0	640	—	
N <sub>2</sub>	720	20,160		
HNO <sub>3</sub>	—	—	31.4	1978.2
H <sub>2</sub> O	3.8	68.4	130.5	2349.0
Total		23,588.4		4327.2

Total, stream (6) + (7) = 23,588.4 + 4327.2 = 27,915.6 kg, checks with inlet stream (4) total of 27,915.

### **Absorber**

In the absorber the NO<sub>2</sub> in the gas stream is absorbed in water to produce acid of about 60 per cent w/w. Sufficient oxygen must be present in the inlet gases to oxidise the NO formed to NO<sub>2</sub>. The rate of oxidation will be dependent on the concentration of oxygen, so an excess is used. For satisfactory operation the tail gases from absorber should contain about 3 per cent O<sub>2</sub> (Miles).



From stream (6) composition:

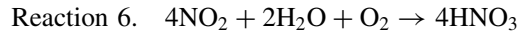
$$\text{NO in inlet stream to absorber} = 15.7 \text{ kmol} \quad \text{and} \quad \text{O}_2 = 20.0 \text{ kmol}$$

*Note:* Though the NO/NO<sub>2</sub> ratio in this stream is not known exactly, this will not affect the calculation of the oxygen required; the oxygen is present in the stream either as free, uncombined oxygen or combined in the NO<sub>2</sub>.

So,  $O_2$  required to oxidise the NO in the inlet to stream to  $NO_2$ , from reaction 4, =  $15.7 \times \frac{1}{2} = 7.85$  kmol.

Hence, the "free" oxygen in the inlet stream =  $20.0 - 7.85 = 12.15$  kmol.

Combining reactions (4) and (5) gives the overall reaction for the absorption of  $NO_2$  to produce  $HNO_3$ .



Using this reaction, the oxygen required to oxidise the NO formed in the absorber can be calculated:

$$\begin{aligned} O_2 \text{ required to oxidise NO formed} &= \{(NO + NO_2) \text{ in stream (6)}\} \times \frac{1}{4} \\ &= (48.9 + 15.7) \times \frac{1}{4} = 16.15 \text{ kmol} \end{aligned}$$

So  $O_2$  required for complete oxidation, in addition to that in inlet gas

$$= 16.15 - 12.15 = 4 \text{ kmol}$$

Let the secondary air flow be  $y$  kmol. Then the  $O_2$  in the secondary air will be =  $0.21 y$  kmol. Of this, 4 kmol react with NO in the absorber, so the free  $O_2$  in the tail gases will be =  $0.21 y - 4$  kmol.

$N_2$  passes through the absorber unchanged, so the  $N_2$  in the tail gases = the  $N_2$  entering the absorber from the cooler-condenser and the secondary air. Hence:

$$N_2 \text{ in tail gas} = 720 + 0.79 y \text{ kmol.}$$

The tail gases are essentially all  $N_2$  and  $O_2$  (the quantity of other constituents is negligible) so the percentage  $O_2$  in the tail gas will be given by:

$$O_2 \text{ per cent} = 3 = \frac{(0.21 y - 4)100}{(720 + 0.79 y) + (0.21 y - 4)}$$

from which

$$y = 141.6 \text{ kmol}$$

and the  $O_2$  in the tail gases =  $141.6 \times 0.21 - 4 = 25.7$  kmol

and the  $N_2$  in the tail gases =  $720 + 111.8 = 831.8$  kmol.

Tail gas composition, the tail gases will contain from 0.2 to 0.3 per cent NO, say 0.2 per cent, then:

$$\begin{aligned} \text{NO in tail gas} &= \text{total flow} \times \frac{0.2}{100} = (N_2 + O_2) \text{ flow} \times 0.002 \\ &= (831.8 + 25.7)0.002 = \underline{\underline{1.7 \text{ kmol}}} \end{aligned}$$

The quantity of the secondary air was based on the assumption that all the nitric oxides were absorbed. This figure will not be changed as it was calculated from an assumed (approximate) value for the concentration of the  $O_2$  in the tail gases. The figure for  $O_2$  in the tail gases must, however, be adjusted to maintain the balance.

The unreacted  $O_2$  can be calculated from Reactions (4) and (6). 1.7 kmol of NO are not oxidised or absorbed, so the adjusted  $O_2$  in tail gases =  $25.7 + 1.7(\frac{1}{4} + \frac{1}{2}) = \underline{\underline{27.0 \text{ kmol}}}$ .

The tail gases will be saturated with water at the inlet water temperature, say 25°C. Partial pressure of water at 25°C = 0.032 atm. The absorber pressure will be approximately 8 atm, so mol fraction water =  $0.032/8 = 4 \times 10^{-3}$  and H<sub>2</sub>O in tail gas =  $857.5 \times 4 \times 10^{-3} = \underline{\underline{3.4 \text{ kmol}}}$ .

Water required, stream (11).

The nitrogen oxides absorbed, allowing for the NO in the tail gases, will equal the HNO<sub>3</sub> formed

$$= (48.9 + 15.7) - 1.7 = 62.9 \text{ kmol} = 3962.7 \text{ kg}$$

Stoichiometric H<sub>2</sub>O required, from reaction 6

$$= \frac{62.9}{4} \times 2 = 31.5 \text{ kmol}$$

The acid strength leaving the absorber will be taken as 60 per cent w/w. Then, water required for dilution

$$= \frac{3962.7}{0.6} \times 0.4 = 2641.8 \text{ kg} = 146.8 \text{ kmol}$$

So, total water required, allowing for the water vapour in the inlet stream (6), but neglecting the small amount in the secondary air

$$= 31.5 + 146.8 + 3.4 - 3.8 = 177.9 \text{ kmol}$$

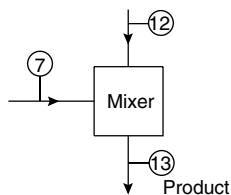
Summary, stream compositions:

Stream	Secondary air (8)		Inlet (9)		Acid (12)		Tail gas (10)		Water feed (11)	
	kmol	kg	kmol	kg	kmol	kg	kmol	kg	kmol	kg
NO	—	—	15.7	471.0	—	—	1.7	51.0	—	—
NO <sub>2</sub>	—	—	48.9	2249.4	trace	—	—	—	—	—
O <sub>2</sub>	29.7	950.4	49.7	1590.4	—	—	27.0	864	—	—
N <sub>2</sub>	111.8	3130.4	831.8	23,290.0	—	—	831.8	23,290.4	—	—
HNO <sub>3</sub>	—	—	—	—	62.9	3962.7	—	—	—	—
H <sub>2</sub> O	trace	—	3.8	68.4	146.8	2641.8	3.4	61.2	177.9	3202.2
Total		4080.8		27,669.2		6604.5		24,266.6		3202.6

Check on totals: Stream (6) + (8) = (9)?  $4080.8 + 23,588.4 = 27,669.2$   
 $27,669.2 = 27,669.2$  checks

Stream (9) + (11) = (10) + (12)?  $27,669.2 + 3203.2 = 24,266.6 + 6604.5$   
 $30,871.4 = 30,871.1$  near enough.

### Acid produced



From cooler-condenser	HNO <sub>3</sub> = 31.4 kmol	= 1978.2 kg
	H <sub>2</sub> O = 130.5 kmol	= 2349.0 kg
From absorber	HNO <sub>3</sub> = 62.9 kmol	= 3962.7 kg
	H <sub>2</sub> O = 146.8 kmol	= 2641.8 kg
Totals	HNO <sub>3</sub> = 1978.2 + 3962.7	= 5940.9 kg
	H <sub>2</sub> O = 2349.0 + 2641.8	= 4990.8 kg
		10,931.7 kg

So, concentration of mixed acids =  $\frac{5940.9}{10,931.7} \times 100 = 54$  per cent.

Summary, stream composition:

Stream	Acid product (13)	
	kmol	kg
HNO <sub>3</sub>	94.3	5940.3
H <sub>2</sub> O	277.3	4990.8
		10,931.7

### **Overall plant yield**

The overall yield can be calculated by making a balance on the combined nitrogen:

$$\text{Yield} = \frac{\text{mols N}_2 \text{ in HNO}_3 \text{ produced}}{\text{mols N}_2 \text{ in NH}_3 \text{ feed}} = \frac{94.3/2}{100/2} = 94.3 \text{ per cent}$$

*Note:* the acid from the cooler-condenser could be added to the acid flow in the absorber, on the appropriate tray, to produce a more concentrated final acid. The secondary air flow is often passed through the acid mixer to strip out dissolved NO.

### **Scale-up to the required production rate**

Production rate, 20,000 t/y HNO<sub>3</sub> (as 100 per cent acid).

With 8000 operating hours per year

$$\text{kg/h} = \frac{20,000 \times 10^3}{8000} = 2500 \text{ kg/h}$$

From calculations on previous basis:

100 kmol NH<sub>3</sub> produces 5940.9 kg HNO<sub>3</sub>.

$$\text{So, scale-up factor} = \frac{2500}{5940.9} = 0.4208$$

To allow for unaccounted physical yield losses, round off to 0.43



All the stream flows, tabulated, were multiplied by this factor and are shown on the flowsheet, Figure 4.2. A sample calculation is given below:

Stream (6) gas from condenser

	Mass 100 kmol NH <sub>3</sub> basis (kg)		Mass flow for 20,000 t/y (kg/h)
NO	471	} × 0.43 =	202.5
NO <sub>2</sub>	2249.4		967.2
O <sub>2</sub>	640.0		275.2
N <sub>2</sub>	20,160.0		8668.0
H <sub>2</sub> O	68.4		29.4
Total	23,588.8		10,143.1

### **Energy balance**

Basis 1 hour.

### **Compressor**

Calculation of the compressor power and energy requirements (see Chapter 3).

$$\text{Inlet flow rate, from flow sheet} = \frac{13,027.7}{29 \times 3600} = 0.125 \text{ kmol/s}$$

Volumetric flow rate

$$\text{at inlet conditions, } 15^\circ\text{C, 1 bar} = 0.125 \times 22.4 \times \frac{288}{273} = 2.95 \text{ m}^3/\text{s}$$

From Figure 3.6, for this flow rate a centrifugal compressor would be used,  $E_p = 74$  per cent.

$$\text{Work (per kmol)} = Z_1 T_1 \mathbf{R} \frac{n}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] \quad (3.31)$$

$$\text{Outlet temperature, } T_2 = T_1 \left( \frac{P_2}{P_1} \right)^m \quad (3.35)$$

As the conditions are well away from the critical conditions for air, equations (3.36a) and (3.38a) can be used

$$m = \frac{(\gamma - 1)}{\gamma E_p} \quad (3.36a)$$

$$n = \frac{1}{1 - m} \quad (3.38a)$$

$\gamma$  for air can be taken as 1.4

$$m = \frac{1.4 - 1}{1.4 \times 0.74} = 0.39$$

$$n = \frac{1}{1 - 0.39} = 1.64$$

The inlet air will be at the ambient temperature, take as 15°C. With no intercooling

$$T_2 = 288 \times 8^{0.39} = \underline{\underline{648 \text{ K}}}$$

This is clearly too high and intercooling will be needed. Assume compressor is divided into two sections, with approximately equal work in each section. Take the intercooler gas outlet temperature as 60°C (which gives a reasonable approach to the normal cooling water temperature of 30°C).

For equal work in each section the interstage pressure

$$= \sqrt{\frac{P_{\text{out}}}{P_{\text{in}}}} = \sqrt{8} = 2.83$$

Taking the interstage pressure as 2.83 atm will not give exactly equal work in each section, as the inlet temperatures are different; however, it will be near enough for the purposes of this example.

$$\begin{aligned} \text{First section work, inlet } 15^\circ\text{C} &= 1 \times 288 \times 8.314 \times \frac{1.64}{1.64 - 1} [(2.83)^{(1.64-1)/1.64} - 1] \\ &= 3072.9 \text{ kJ/kmol} \end{aligned}$$

$$\begin{aligned} \text{Second section work, inlet } 60^\circ\text{C} &= 1 \times 333 \times 8.314 \times \frac{1.64}{1.64 - 1} [(2.83)^{(1.64-1)/1.64} - 1] \\ &= 3552.6 \text{ kJ/kmol} \end{aligned}$$

$$\text{Total work} = 3072.9 + 3552.6 = 6625.5 \text{ kJ/kmol}$$

$$\begin{aligned} \text{Compressor power} &= \frac{\text{work/kmol} \times \text{kmol/s}}{\text{efficiency}} = \frac{6625.5 \times 0.125}{0.74} \\ &= 1119 \text{ kJ/s} = 1.12 \text{ MW} \end{aligned}$$

$$\text{Energy required per hour} = 1.12 \times 3600 = 4032 \text{ MJ}$$

$$\begin{aligned} \text{Compressor outlet temperature} &= 333(2.83)^{0.39} = 500 \text{ K} \\ &\text{say, } 230^\circ\text{C} \end{aligned}$$

This temperature will be high enough for no preheating of the reactor feed to be needed (Strelzoff).

### ***Ammonia vaporiser***

The ammonia will be stored under pressure as a liquid. The saturation temperature at 8 atm is 20°C. Assume the feed to the vaporiser is at ambient temperature, 15°C.

$$\text{Specific heat at 8 bar} = 4.5 \text{ kJ/kgK}$$

$$\text{Latent heat at 8 bar} = 1186 \text{ kJ/kg}$$

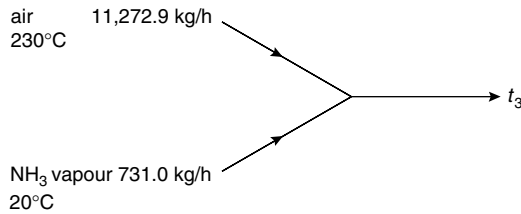
$$\text{Flow to vaporiser} = 731.0 \text{ kg/h}$$

Heat input required to raise to 20°C and vaporise

$$= 731.0[4.5(20 - 15) + 1186] = 883,413.5 \text{ kJ/h}$$

$$\text{add 10 per cent for heat losses} = 1.1 \times 883,413.5 = 971,754.9 \text{ kJ/h}$$

$$\text{say, } 972 \text{ MJ}$$

**Mixing tee**

$C_p$  air = 1 kJ/kgK,

$C_p$  ammonia vapour 2.2 kJ/kgK.

*Note:* as the temperature of the air is only an estimate, there is no point in using other than average values for the specific heats at the inlet temperatures.

Energy balance around mixing tee, taking as the datum temperature the inlet temperature to the oxidiser,  $t_3$ .

$$11,272.9 \times 1(230 - t_3) + 731 \times 2.2(20 - t_3) = 0$$

$$t_3 = 204^\circ\text{C}$$

**Oxidiser**

The program ENERGY 1 (see Chapter 3) was used to make the balance over on the oxidiser. Adiabatic operation was assumed (negligible heat losses) and the outlet temperature found by making a series of balances with different outlet temperatures to find the value that reduced the computed cooling required to zero (adiabatic operation). The data used in the program are listed below:

$$\Delta H_r^\circ \text{ reaction 1} = -226,334 \text{ kJ/kmol (per kmol NH}_3 \text{ reacted)}$$

$$\Delta H_r^\circ \text{ reaction 2} = -316,776 \text{ kJ/kmol (per kmol NH}_3 \text{ reacted)}$$

All the reaction yield losses were taken as caused by reaction 2.

NH<sub>3</sub> reacted, by reaction 1

$$\text{Flow of NH}_3 \text{ to oxidiser} \times \text{reactor yield} = \frac{731.0 \times 0.96}{17} = 41.3 \text{ kmol/h}$$

$$\text{balance by reaction 2} = \frac{731.0 \times 0.04}{17} = 1.7 \text{ kmol/h}$$

Summary, flows and heat capacity data:

Stream component	Feed (3) kmol/h	Product (4) kmol/h	$C_p^\circ$ kJ/kmol K			
			<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
NH <sub>3</sub>	43	—	27.32	23.83E-3	17.07E-6	-11.85E-9
O <sub>2</sub>	82.1	29.2	28.11	-3.68E-6	17.46E-6	-10.65E-9
N <sub>2</sub>	308.7	309.6	31.15	-1.36E-2	26.80E-6	-11.68E-9
NO	—	41.3	29.35	-0.94E-3	9.75E-6	-4.19E-9
H <sub>2</sub> O	—	64.5	32.24	19.24E-4	10.5E-6	-3.60E-9
Temp. K	477	$T_4$				

The outlet temperature  $T_4$  was found to be 1180 K = 907°C.

**Waste-heat boiler (WHB)**

As the amount of NO oxidised to NO<sub>2</sub> in this unit has not been estimated, it is not possible to make an exact energy balance over the unit. However, the maximum possible quantity of steam generated can be estimated by assuming that all the NO is oxidised; and the minimum quantity by assuming that none is. The plant steam pressure would be typically 150 to 200 psig  $\approx$  11 bar, saturation temperature 184°C. Taking the approach temperature of the outlet gases (difference between gas and steam temperature) to be 50°C, the gas outlet temperature will be = 184 + 50 = 234°C (507 K).

From the flow-sheet, NO entering WHB =  $\frac{1238.4}{30} = 41.3$  kmol

$$\text{O}_2 \text{ entering} = \frac{935.7}{32} = 29.2 \text{ kmol/h}$$

If all the NO is oxidised, reaction 4, the oxygen leaving the WHB will be reduced to

$$29.2 - \frac{41.3}{2} = 8.6 \text{ kmol/h}$$

$$\Delta H_r^\circ = -57,120 \text{ kJ/kmol, NO oxidised}$$

If no NO is oxidised the composition of the outlet gas will be the same as the inlet. The inlet gas has the same composition as the reactor outlet, which is summarised above. Summarised below are the flow changes if the NO is oxidised:

		$C_p^\circ$ (kJ/kmol K)			
	(kmol/h)	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
O <sub>2</sub>	7.46			as above	
NO <sub>2</sub>	41.3	24.23	4.84 E-2	-20.81 E-2	0.29 E-9
Temp.	507K				

Using the program ENERGY 1, the following values were calculated for the heat transferred to the steam:

$$\begin{aligned} \text{no NO oxidised} & \quad 9.88 \text{ GJ/h} \\ \text{all NO oxidised} & \quad 12.29 \text{ GJ/h} \end{aligned}$$

Steam generated; take feed water temperature as 20°C,

$$\text{enthalpy of saturated steam at 11 bar} = 2781 \text{ kJ/kg}$$

$$\text{enthalpy of water at 20°C} = 84 \text{ kJ/kg}$$

$$\text{heat to form 1 kg steam} = 2781 - 84 = 2697 \text{ kJ}$$

$$\text{steam generated} = \frac{\text{heat transferred}}{\text{enthalpy change per kg}}$$

$$\text{so, minimum quantity generated} = \frac{9,880,000}{2697} = 3662 \text{ kg/h}$$

$$\text{maximum} = \frac{12,290,000}{2697} = 4555 \text{ kg/h}$$

*Note:* in practice superheated steam would probably be generated, for use in a turbine driving the air compressor.

### **Cooler-condenser**

The sources of heat to be considered in the balance on this unit are:

1. Sensible heat: cooling the gases from the inlet temperature of 234°C to the required outlet temperature (the absorber inlet temperature) 40°C.
2. Latent heat of the water condensed.
3. Exothermic oxidation of NO to NO<sub>2</sub>.
4. Exothermic formation of nitric acid.
5. Heat of dilution of the nitric acid formed, to 40 per cent w/w.
6. Sensible heat of the outlet gas and acid streams.

So that the magnitude of each source can be compared, each will be calculated separately. Take the datum temperature as 25°C.

#### **1. Gas sensible heat**

The program ENERGY 1 was used to calculate the sensible heat in the inlet and outlet gas streams. The composition of the inlet stream and the heat capacity data will be the same as that for the WHB outlet given above. Outlet stream flows from flow-sheet, converted to kmol/h:

Condenser outlet (6)	
	kmol/h
O <sub>2</sub>	8.6
N <sub>2</sub>	309.6
NO	6.75
NO <sub>2</sub>	21.03
H <sub>2</sub> O	1.63
Temp. 313 K	

Sensible heat inlet stream (5) = 2.81 GJ/h,  
outlet stream (6) = 0.15 GJ/h.

#### **2. Condensation of water**

Water condensed = (inlet H<sub>2</sub>O – outlet H<sub>2</sub>O) = (1161 – 29) = 1131.6 kg/h  
Latent heat of water at the inlet temperature, 230°C = 1812 kJ/kg

The steam is considered to condense at the inlet temperature and the condensate then cooled to the datum temperature.

$$\begin{aligned} \text{Heat from condensation} &= 1131.6 \times 1812 = 2.05 \times 10^6 \text{ kJ/h} \\ \text{Sensible heat to cool condensate} &= 1131.6 \times 4.18(230 - 25) \\ &= 0.97 \times 10^6 \text{ kJ/h} \\ \text{Total, condensation and cooling} &= (2.05 + 0.97)10^6 \text{ kJ/h} \\ &= 3.02 \text{ GJ/h} \end{aligned}$$

### 3. Oxidation of NO

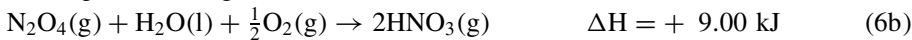
The greatest heat load will occur if all the oxidation occurs in the cooler-condenser (i.e. none in the WHB) which gives the worst condition for the cooler-condenser design.

$$\begin{aligned}\text{Mols of NO oxidised} &= \text{mols in} - \text{mols out} = 41.3 - 6.75 = 34.55 \text{ kmol/h} \\ \text{From reaction 4, heat generated} &= 34.55 \times 57,120 \\ &= 1.97 \times 10^6 \text{ kJ/h} = 1.97 \text{ GJ/h}\end{aligned}$$

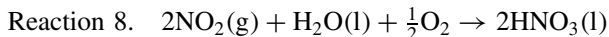
### 4. Formation of nitric acid

$$\text{HNO}_3 \text{ formed, from flow sheet,} = \frac{850.6}{63} = 13.50 \text{ kmol/h}$$

The enthalpy changes in the various reactions involved in the formation of aqueous nitric acid are set out below (Miles):



Combining reactions 6a, 6b and 7.



$$\begin{aligned}\text{overall enthalpy change} &= -57.32 + 9.00 + 2(-39.48) \\ &= -127.28 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\text{heat generated per kmol of HNO}_3(\text{l}) \text{ formed} &= \frac{127.28}{2} \times 10^3 \\ &= 63,640 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\text{heat generated} &= 13.50 \times 63,640 = 0.86 \times 10^6 \text{ kJ/h} \\ &= 0.86 \text{ GJ/h}\end{aligned}$$

Note, the formation of  $\text{N}_2\text{O}_4$  and the part played by  $\text{N}_2\text{O}_4$  in the formation of nitric acid was not considered when preparing the flow-sheet, as this does not affect the calculation of the components flow-rates.

### 5. Heat of dilution of $\text{HNO}_3$

The heat of dilution was calculated from an enthalpy—concentration diagram given in Perry's *Chemical Engineers Handbook*, 5th edn, p. 3.205, Figure 3.42.

The reference temperature for this diagram is 32°F (0°C). From the diagram:

$$\begin{aligned}\text{enthalpy of 100 per cent HNO}_3 &= 0 \\ \text{enthalpy of 45 per cent HNO}_3 &= -80 \text{ Btu/lb solution} \\ \text{specific heat 45 per cent HNO}_3 &= 0.67\end{aligned}$$

So, heat released on dilution, at 32°F =  $80 \times 4.186/1.8 = 186 \text{ kJ/kg soln.}$

$$\begin{aligned}\text{Heat to raise solution to calculation datum temperature of } 25^\circ\text{C} &= 0.67(25 - 0)4.186 \\ &= 70.1 \text{ kJ/kg.}\end{aligned}$$

So, heat generated on dilution at 25°C =  $186 - 70.1 = 115.9 \text{ kJ/kg soln.}$

$$\begin{aligned} \text{Quantity of solution produced by dilution of 1 kmol 100 per cent HNO}_3 &= \frac{63}{45} \times 100 \\ &= 140 \text{ kg,} \end{aligned}$$

so, heat generated on dilution of 1 kmol =  $140 \times 115.9 = 16,226 \text{ kJ}$ ,

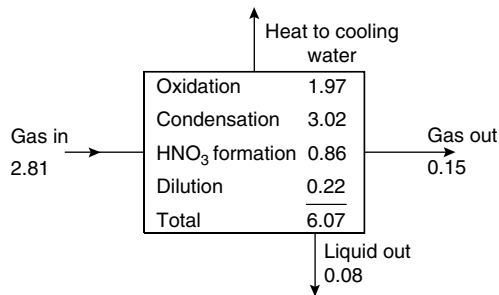
$$\begin{aligned} \text{so, total heat generated} &= 13.5 \times 16,226 = 219,051 \text{ kJ/h} \\ &= 0.22 \text{ GJ/h.} \end{aligned}$$

### 6. Sensible heat of acid

Acid outlet temperature was taken as  $40^\circ\text{C}$ , which is above the datum temperature.

$$\text{Sensible heat of acid} = 0.67 \times 4.186(40 - 25) \times 1860.7 = 78,278 \text{ kJ/h} = 0.08 \text{ GJ/h}$$

### Heat balance (GJ/h)



$$\begin{aligned} \text{Heat transferred to cooling water} &= 2.81 + 6.07 - 0.15 - 0.08 \\ &= 8.65 \text{ GJ/h} \end{aligned}$$

### Air cooler

The secondary air from the compressor must be cooled before mixing with the process gas stream at the absorber inlet; to keep the absorber inlet temperature as low as possible. Take the outlet temperature as the same as exit gases from the cooler condenser,  $40^\circ\text{C}$ .

Secondary air flow, from flow-sheet, 1754.8 kg/h

Specific heat of air 1 kJ/kgK

$$\begin{aligned} \text{Heat removed from secondary air} &= 1754.8 \times 1 \times (230 - 40) \\ &= 333,412 \text{ kJ/h} = 0.33 \text{ GJ/h} \end{aligned}$$

### Absorber

The sources of heat in the absorber will be the same as the cooler-condenser and the same calculation methods have been used. The results are summarised below:

Sensible heat in inlet gases from cooler-condenser = 0.15 GJ/h

Sensible heat in secondary air =  $1754.8 \times 1.0(40 - 25) = 0.018 \text{ GJ/h}$

Sensible heat in tail gases (at datum) = 0

Sensible heat in water feed (at datum) = 0

$$\text{NO oxidised} = \frac{202.5 - 21.9}{30} = 6.02 \text{ kmol/h}$$

$$\text{Heat generated} = 6.02 \times 57,120 = 0.34 \text{ GJ/h}$$

$$\text{HNO}_3 \text{ formed} = \frac{1704}{63} = 27.05 \text{ kmol/h}$$

$$\text{Heat generated} = 27.05 \times 63,640 = 1.72 \text{ GJ/h}$$

$$\text{Heat of dilution to 60 per cent at } 25^\circ\text{C} = 27.05 \times 14,207 = 0.38 \text{ GJ/h}$$

$$\text{Water condensed} = 29.4 - 26.3 = 3.1 \text{ kg/h}$$

$$\text{Latent heat at } 40^\circ\text{C} = 2405 \text{ kJ/h}$$

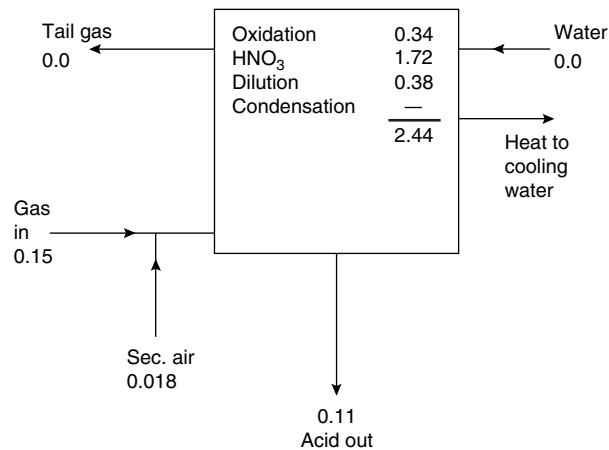
$$\text{Sensible heat above datum temperature} = 4.18 (40 - 25) = 63 \text{ kJ/kg}$$

$$\text{Heat released} = 3.1(2405 + 63) = 7.6 \times 10^{-3} \text{ GJ/h (negligible)}$$

$$\text{Sensible heat in acid out, specific heat 0.64, take temperature out as same as gas inlet, } 40^\circ\text{C}$$

$$= 0.64(40 - 25)4.18 \times 2840 = 0.11 \text{ GJ/h}$$

### Heat balance (GJ/h)



$$\text{Heat transferred to cooling water} = 0.15 + 0.018 + 2.44 - 0.11 = \underline{\underline{2.5 \text{ GJ/h}}}$$

### Mixer

Calculation of mixed acid temperature.

Taking the datum as  $0^\circ\text{C}$  for this calculation, so the enthalpy-concentration diagram can be used directly.

From diagram:

$$\text{enthalpy 45 per cent acid at } 0^\circ\text{C} = -186 \text{ kJ/kg}$$

$$\text{specific heat} = 0.67 \text{ kcal/kg}^\circ\text{C}$$

$$\text{enthalpy 60 per cent acid at } 0^\circ\text{C} = -202 \text{ kJ/kg}$$

$$\text{specific heat} = 0.64 \text{ kcal/kg}^\circ\text{C}$$



So, enthalpy 45 per cent acid at 40°C =  $-186 + 0.67 \times 4.186(40) = -73.8$  kJ/kg  
 and enthalpy 60 per cent acid at 40°C =  $-202 + 0.64 \times 4.186(40) = -94.8$  kJ/kg

$$\begin{aligned} \text{Enthalpy of mixed acid} &= \frac{(-73.8 \times 1860.7) + (-94.8 \times 2840.0)}{(1860.7 + 2840.0)} \\ &= -86.5 \text{ kJ/kg} \end{aligned}$$

From enthalpy-concentration diagram, enthalpy of mixed acid  
 (54 per cent) at 0°C =  $-202$  kJ/kg; specific heat =  $0.65$  kcal/kg°C  
 so, "sensible" heat in mixed acid above datum of 0°C

$$= -86.5 - (-202) = 115.5 \text{ kJ/kg}$$

$$\text{and, mixed acid temperature} = \frac{115.5}{0.65 \times 4.186} = 43^\circ\text{C}$$

### ***Energy recovery***

In an actual nitric acid plant the energy in the tail gases would normally be recovered by expansion through a turbine coupled to the air compressor. The tail gases would be preheated before expansion, by heat exchange with the process gas leaving the WHB.

## **4.4. COMPUTER-AIDED FLOW-SHEETING**

The computer programs available for flow-sheeting in process design can be classified into two basic types:

1. Full simulation programs, which require powerful computing facilities.
2. Simple material balance programs requiring only a relatively small core size.

The full simulation programs are capable of carrying out rigorous simultaneous heat and material balances, and preliminary equipment design: producing accurate and detailed flow-sheets. In the early stages of a project the use of a full simulation package is often not justified and a simple material balance program is more suitable. These are an aid to manual calculations and enable preliminary flow-sheets to be quickly, and cheaply, produced.

## **4.5. FULL STEADY-STATE SIMULATION PROGRAMS**

Complex flow-sheeting programs, that simulate the operation and a complete process, or individual units, have been developed by several commercial software organisations. The names of the principal packages available, and the contact address, are listed in Table 4.1. Many of the commercial programs have been made available by the proprietors to university and college departments for use in teaching, at nominal cost.

Table 4.1. Simulation packages

Acronym	Type	Source	Internet address http/www.—
ASPEN	steady-state	Aspen Technology Inc. Ten Canal Park, Cambridge, MA 02141-2201, USA	Aspentech.com
Aspen DPS			
DESIGN II	steady-state	WinSim Inc. P.O. Box 1885, Houston, TX 77251-1885, USA	winsim.com
HYSYS	steady-state	Hyprotech Suite 900, 125-9 Avenue SE, Calgary, Alberta, T2G-OP6, Canada	hyprotech.com
	dynamic	Merged with Aspen Tech	
PRO/II	steady-state	SimSci-Esscor 5760 Fleet Street, Suite 100, Carlsbad, CA 92009, USA	simsci.com
DYNSIM	dynamic		
CHEMCAD	steady-state	Chemstations Inc. 2901 Wilcrest, Suite 305, Houston, TX 77042 USA	chemstations.net

Note: Contact the web site to check the full features of the current versions of the programs.

Detailed discussion of these programs is beyond the scope of this book. For a general review of the requirements, methodology and application of process simulation programs the reader is referred to the books by: Husain (1986), Wells and Rose (1986), Leesley (1982), Benedek (1980), Mah and Seider (1980), Westerberg *et al.* (1979) and Crowe *et al.* (1971); and the paper by Panelides (1988).

Process simulation programs can be divided into two basic types:

*Sequential-modular* programs: in which the equations describing each process unit (module) are solved module-by-module in a stepwise manner; and iterative techniques used to solve the problems arising from the recycle of information.

They simulate the steady-state operation of the process and can be used to draw-up the process flow sheet, and to size individual items of equipment, such as distillation columns.

*Equation based* programs: in which the entire process is described by a set of differential equations, and the equations solved simultaneously: not stepwise, as in the sequential approach. Equation based programs can simulate the unsteady-state operation of processes and equipment.

In the past, most simulation programs available to designers were of the sequential-modular type. They were simpler to develop than the equation based programs, and required only moderate computing power. The modules are processed sequentially, so essentially only the equations for a particular unit are in the computer memory at one time. Also, the process conditions, temperature, pressure, flow-rate, are fixed in time.

But, computational difficulties can arise due to the iterative methods used to solve recycle problems and obtain convergence. A major limitation of modular-sequential simulators is the inability to simulate the dynamic, time dependent, behaviour of a process.

Equation based, dynamic, simulators require appreciably more computing power than steady-state simulators; to solve the thousands of differential equations needed to describe a process, or even a single item of equipment. However, with the development of fast powerful machines this is no longer a restriction. By their nature, equation based programs do not experience the problems of recycle convergence inherent in sequential simulators. But, as temperature, pressure and flow-rate are not fixed and the input of one unit is not determined by the calculated output from the previous unit in the sequence, as with steady-state simulators, equation based programs are more time demanding on computer time. This has led to the development of hybrid programs in which the steady-state simulator is used to generate the initial conditions for the dynamic simulation.

The principal advantage of equation based, dynamic, simulators is their ability to model the unsteady-state conditions that occur at start-up and during fault conditions. Dynamic simulators are being increasingly used for safety studies and in the design of control systems.

The structure of a typical simulation program is shown in Figure 4.4.

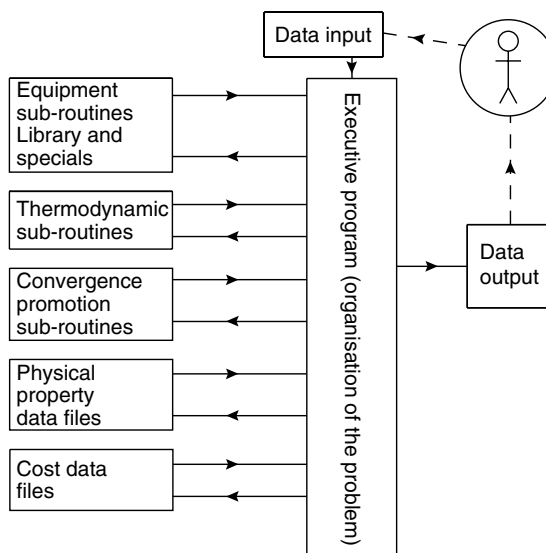


Figure 4.4. A typical simulation program

The program consists of:

1. A main executive program; which controls and keeps track of the flow-sheet calculations and the flow of information to and from the sub-routines.

2. A library of equipment performance sub-routines (modules); which simulate the equipment and enable the output streams to be calculated from information on the inlet streams.
3. A data bank of physical properties. To a large extent the utility of a sophisticated flow-sheeting program will depend on the comprehensiveness of the physical property data bank. The collection of the physical property data required for the design of a particular process, and its transformation into a form suitable for a particular flow-sheeting program can be very time-consuming.
4. Sub-programs for thermodynamic routines; such as the calculation of vapour-liquid equilibria and stream enthalpies.
5. Sub-programs and data banks for costing; the estimation of equipment capital costs and operating costs. Full simulation flow-sheeting programs enable the designer to consider alternative processing schemes, and the cost routines allow quick economic comparisons to be made. Some programs include optimisation routines. To make use of a costing routine, the program must be capable of producing at least approximate equipment designs.

In a sequential-modular program the executive program sets up the flow-sheet sequence, identifies the recycle loops, and controls the unit operation calculations: interacting with the unit operations library, physical property data bank and the other sub-routines. It will also contain procedures for the optimum ordering the calculations and routines to promote convergence.

In an equation based simulators the executive program sets up the flow-sheet and the set of equations that describe the unit operations, and then solves the equations; taking data from the unit operations library and physical property data bank and the file of thermodynamic sub-routines.

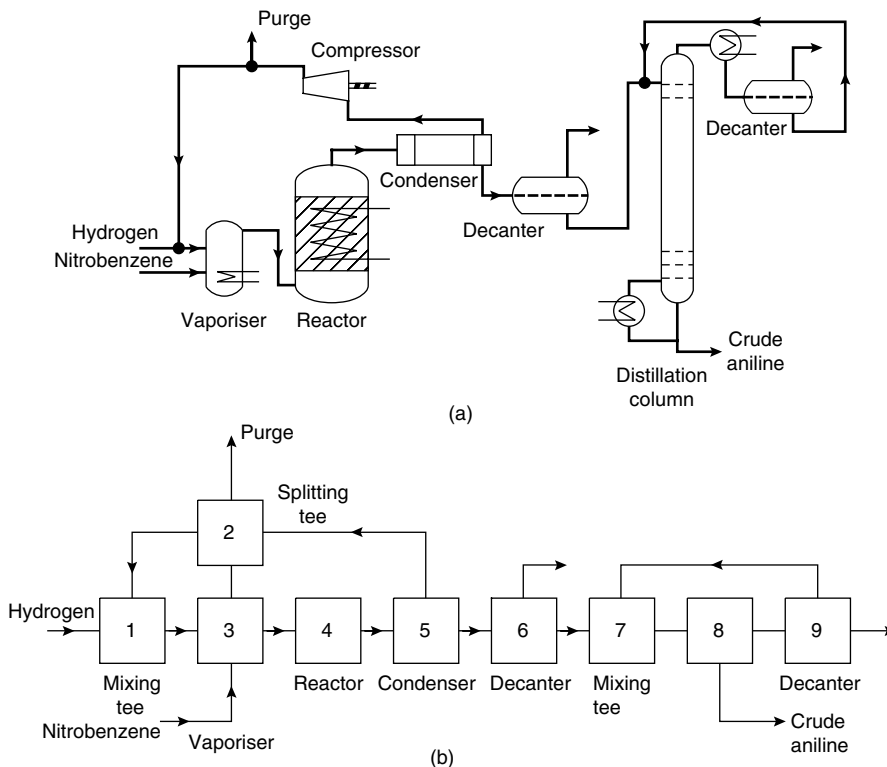
Many of the proprietary flow-sheeting packages are now front-ended with a graphical user interface to display the flow-sheet and facilitate the input of information to the package.

#### **4.5.1. Information flow diagrams**

To present the problem to the computer, the basic process flow diagram, which shows the sequence of unit operations and stream connections, must be transformed into an information flow diagram, such as that shown in Figure 4.5*b*. Each block represents a calculation module in the simulation program; usually a process unit or part of a unit. Units in which no change of composition, or temperature or pressure, occurs are omitted from the information flow diagram. But other operations not shown on the process flow diagram as actual pieces of equipment, but which cause changes in the stream compositions, such as mixing tees, must be shown.

The lines and arrows connecting the blocks show the flow of information from one subprogram to the next. An information flow diagram is a form of directed graph (a diagraph).

The calculation topology defined by the information diagram is transformed into a numerical form suitable for input into the computer, usually as a matrix.



Note: (1) Modules have been added to represent mixing and separation tees.  
 (2) The compressor is omitted.  
 (3) The distillation module includes the condenser and reboiler.

Figure 4.5. (a) Process flow diagram: hydrogenation of nitrobenzene to aniline (b) Information flow diagram hydrogenation of nitrobenzene to aniline (Figure 4.5a)

## 4.6. MANUAL CALCULATIONS WITH RECYCLE STREAMS

If a proprietary simulation program is not available, problems involving recycle streams can be solved on a spreadsheet using the procedure described below.

The procedure is based on the theory of recycle processes published by Nagiev (1964). The concept of split-fractions is used to set up the set of simultaneous equations that define the material balance for the process. This method has also been used by Rosen (1962) and is described in detail in the book by Henley and Rosen (1969).

### 4.6.1. The split-fraction concept

In an information flow diagram, such as that shown in Figure 4.5b, each block represents a calculation module; that is, the set of equations that relate the outlet stream component flows to the inlet flows. The basic function of most chemical processing units (unit operations) is to divide the inlet flow of a component between two or more outlet

streams; for example, a distillation column divides the components in the feed between the overhead and bottom product streams, and any side streams. It is therefore convenient, when setting up the equations describing a unit operation, to express the flow of any component in any outlet stream as a fraction of the flow of that component in the inlet stream.

The block shown in Figure 4.6 represents any unit in an information flow diagram, and shows the nomenclature that will be used in setting up the material balance equations.

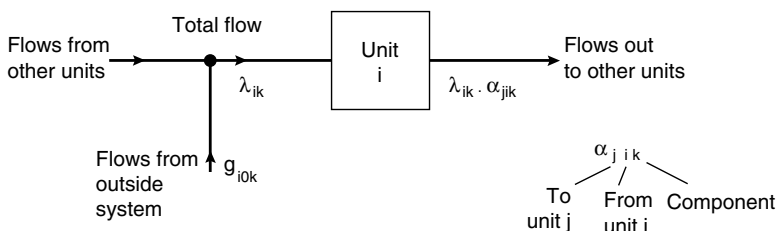


Figure 4.6.

- $i$  = the unit number,
- $\lambda_{i,k}$  = the total flow into the unit  $i$  of the component  $k$ ,
- $\alpha_{j,i,k}$  = the fraction of the total flow of component  $k$  entering unit  $i$  that leaves in the outlet stream connected to the unit  $j$ ; the “split-fraction coefficient”,
- $g_{i,0,k}$  = any fresh feed of component  $k$  into unit  $i$ ; flow from outside the system (from unit 0).

The flow of any component from unit  $i$  to unit  $j$  will equal the flow into unit  $i$  multiplied by the split-fraction coefficient.

$$= \lambda_{i,k} \times \alpha_{j,i,k}$$

The value of the split-fraction coefficient will depend on the nature of the unit and the inlet stream composition.

The outlet streams from a unit can feed forward to other units, or backward (recycle).

An information flow diagram for a process consisting of three units, with two recycle streams is shown in Figure 4.7. The nomenclature defined in Figure 4.6 is used to show the stream flows.

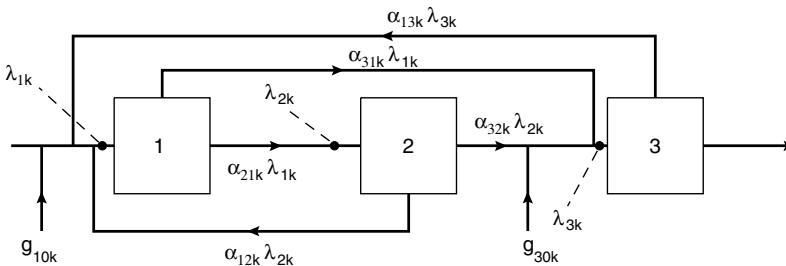


Figure 4.7.

Consider the streams entering unit 1.

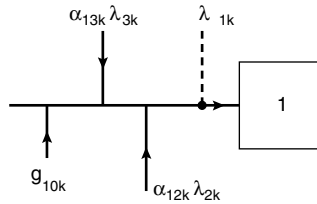


Figure 4.8.

A material balance gives:

$$g_{10k} + \alpha_{13k} \lambda_{3k} + \alpha_{12k} \lambda_{2k} = \lambda_{1k} \tag{4.1}$$

A similar material balance can be written at the inlet to each unit:

$$\text{unit 2: } \alpha_{21k} \lambda_{1k} = \lambda_{2k} \tag{4.2}$$

$$\text{unit 3: } \alpha_{32k} \lambda_{2k} + g_{30k} + \alpha_{31k} \lambda_{1k} = \lambda_{3k} \tag{4.3}$$

Rearranging each equation

$$\lambda_{1k} - \alpha_{12k} \lambda_{2k} - \alpha_{13k} \lambda_{3k} = g_{10k} \tag{4.1a}$$

$$-\alpha_{21k} \lambda_{1k} + \lambda_{2k} = 0 \tag{4.2b}$$

$$-\alpha_{31k} \lambda_{1k} - \alpha_{32k} \lambda_{2k} + \lambda_{3k} = g_{30k} \tag{4.3c}$$

This is simply a set of three simultaneous equations in the unknown flows  $\lambda_{1k}, \lambda_{2k}, \lambda_{3k}$ .

These equations are written in matrix form:

$$\begin{matrix}
 & & & i \\
 & & & 1 & 2 & 3 \\
 j & 1 & \begin{bmatrix} 1 & -\alpha_{12k} & -\alpha_{13k} \\ -\alpha_{21k} & 1 & 0 \\ -\alpha_{31k} & -\alpha_{32k} & 1 \end{bmatrix} & \times & \begin{bmatrix} \lambda_{1k} \\ \lambda_{2k} \\ \lambda_{3k} \end{bmatrix} & = & \begin{bmatrix} g_{10k} \\ 0 \\ g_{30k} \end{bmatrix}
 \end{matrix}$$

There will be a set of such equations for each component.

This procedure for deriving the set of material balance equations is quite general. For a process with  $n$  units there will be a set of  $n$  equations for each component.

The matrix form of the  $n$  equations will be as shown in Figure 4.9.

$$\begin{bmatrix} (1 - \alpha_{11k}) - \alpha_{12k} & -\alpha_{13k} & \dots & -\alpha_{1nk} \\ -\alpha_{21k} & (1 - \alpha_{22k}) - \alpha_{23k} & \dots & -\alpha_{2nk} \\ \dots & \dots & \dots & \dots \\ -\alpha_{n1k} & \dots & \dots & (1 - \alpha_{nnk}) \end{bmatrix} \times \begin{bmatrix} \lambda_{1k} \\ \lambda_{2k} \\ \dots \\ \lambda_{nk} \end{bmatrix} = \begin{bmatrix} g_{10k} \\ g_{20k} \\ \dots \\ g_{n0k} \end{bmatrix}$$

Figure 4.9. Matrix form of equations for  $n$  units

For practical processes most of the split-fraction coefficients are zero and the matrix is sparse.

In general, the equations will be non-linear, as the split-fractions coefficients ( $\alpha$ 's) will be functions of the inlet flows, as well as the unit function. However, many of the coefficients will be fixed by the process constraints, and the remainder can usually be taken as independent of the inlet flows ( $\lambda$ 's) as a first approximation.

The fresh feeds will be known from the process specification; so if the split-fraction coefficients can be estimated, the equations can be solved to determine the flows of each component to each unit. Where the split-fractions are strongly dependent on the inlet flows, the values can be adjusted and the calculation repeated until a satisfactory convergence between the estimated values and those required by the calculated inlet flows is reached.

### **Processes with reaction**

In a chemical reactor, components in the inlet streams are consumed and new components, not necessarily in the inlet streams, are formed. The components formed cannot be shown as split-fractions of the inlet flows and must therefore be shown as pseudo fresh-feeds.

A reactor is represented as two units (Figure 4.10). The split-fractions for the first unit are chosen to account for the loss of material by reaction. The second unit divides the reactor output between the streams connected to the other units. If the reactor has only one outlet stream (one connection to another unit), the second unit forming the reactor can be omitted.

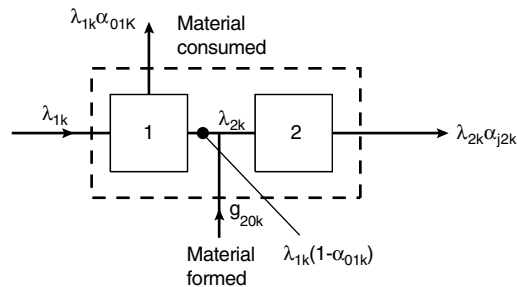


Figure 4.10. Reactor unit

### **Closed recycle systems**

In some processes, a component may be recycled around two or more units in a closed loop. For example, the solvent in an absorption or liquid extraction process will normally be recovered by distillation and recycled. In this situation it will be necessary to introduce the solvent as a pseudo fresh-feed and to remove it from the recycle loop by introducing a dummy stream divider, purging one stream.

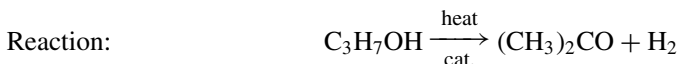
As, in practice, some of the recycling component will always be lost, the amount purged should be adjusted to allow for any losses that are identified on the flow-sheet.



### 4.6.2. Illustration of the method

The procedure for setting up the equations and assigning suitable values to the split-fraction coefficients is best illustrated by considering a short problem: the manufacture of acetone from isopropyl alcohol.

#### **Process description**



Isopropyl alcohol is vaporised, heated and fed to a reactor, where it undergoes catalytic dehydrogenation to acetone. The reactor exit gases (acetone, water, hydrogen and unreacted isopropyl alcohol) pass to a condenser where most of the acetone, water and alcohol condense out. The final traces of acetone and alcohol are removed in a water scrubber. The effluent from the scrubber is combined with the condensate from the condenser, and distilled in a column to produce “pure” acetone and an effluent consisting of water and alcohol. This effluent is distilled in a second column to separate the excess water. The product from the second column is an azeotrope of water and isopropyl alcohol containing approximately 91 per cent alcohol. This is recycled to the reactor. Zinc oxide or copper is used as the catalyst, and the reaction carried out at 400 to 500°C and 40 to 50 psig pressure (4.5 bar). The yield to acetone is around 98 per cent, and the conversion of isopropyl alcohol per pass through the reactor is 85 to 90 per cent.

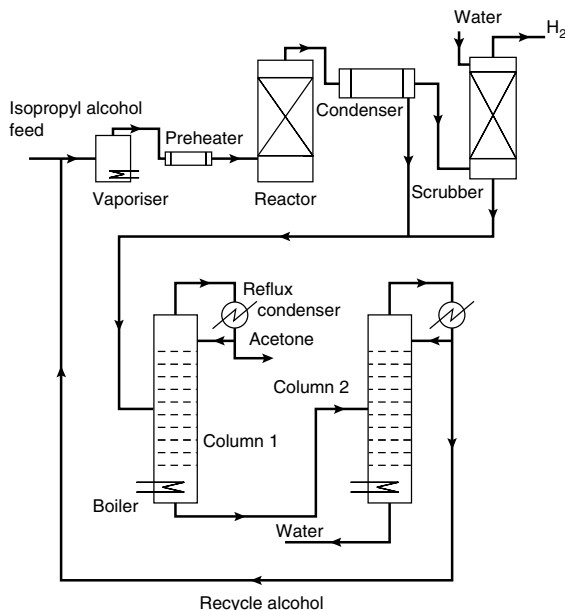


Figure 4.11. Process flow diagram

The process flow diagram is shown in Figure 4.11. This diagram is simplified and drawn as an information flow diagram in Figure 4.12. Only those process units in which there is a difference in composition between the inlet and outlet streams are shown. The

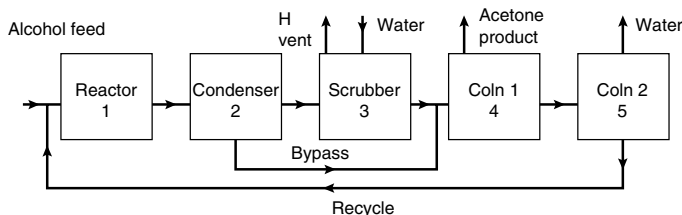


Figure 4.12. Information flow diagram

preheater and vaporiser are not shown, as there is no change in composition in these units and no division of the inlet stream into two or more outlet streams.

Figure 4.12 is redrawn in Figure 4.13, showing the fresh feeds, split-fraction coefficients and component flows. Note that the fresh feed  $g_{20k}$  represents the acetone and hydrogen generated in the reactor. There are 5 units so there will be 5 simultaneous equations. The equations can be written out in matrix form (Figure 4.14) by inspection of Figure 4.13. The fresh feed vector contains three terms.

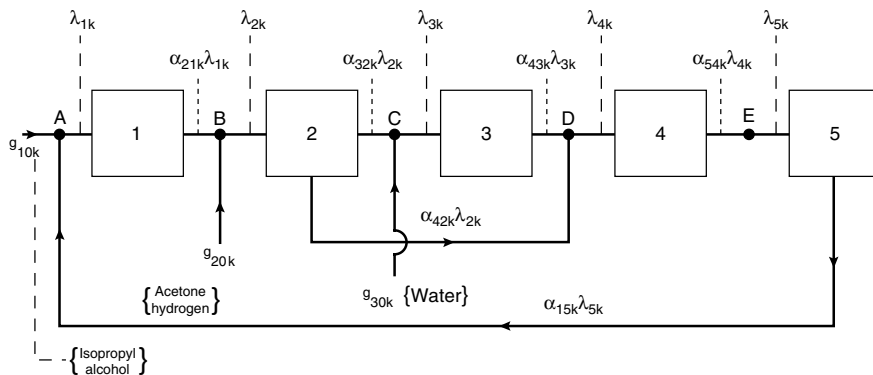


Figure 4.13. Split-fractions and fresh feeds

	1	2	3	4	5				
1	1	0	0	0	$-\alpha_{15k}$	$\times$	$\begin{bmatrix} \lambda_{1k} \\ \lambda_{2k} \\ \lambda_{3k} \\ \lambda_{4k} \\ \lambda_{5k} \end{bmatrix}$	$=$	$\begin{bmatrix} g_{10k} \\ g_{20k} \\ g_{30k} \\ 0 \\ 0 \end{bmatrix}$
2	$-\alpha_{21k}$	1	0	0	0				
3	0	$-\alpha_{32k}$	1	0	0				
4	0	$-\alpha_{42k}$	$-\alpha_{43k}$	1	0				
5	0	0	0	$-\alpha_{54k}$	1				

Figure 4.14. The set of equations

### Estimation of the split-fraction coefficients

The values of the split-fraction coefficients will depend on the function of the processing unit and the constraints on the stream flow-rates and compositions. Listed below are suggested first trial values, and the basis for selecting the particular value for each component.

*Component 1, isopropyl alcohol ( $k = 1$ )*

- Unit 1, Reactor. The conversion per pass is given as 90 per cent, so for each mol entering only 10 per cent leave, hence  $\alpha_{211}$  is fixed at 0.1. For this example it is assumed that the conversion is independent of the feed stream composition.
- Unit 2, Condenser. Most of the alcohol will condense as its boiling point is 82°C. Assume 90 per cent condensed,  $\alpha_{421} = 0.9$  (liquid out) and  $\alpha_{321} = 0.1$  (vapour out). The actual amounts will depend on the condenser design.
- Unit 3, Scrubber. To give a high plant yield, the scrubber would be designed to recover most of the alcohol in the vent stream. Assume 99 per cent recovery, allowing for the small loss that must theoretically occur,  $\alpha_{431} = 0.99$ .
- Unit 4, First column. The fraction of alcohol in the overheads would be fixed by the amount allowed in the acetone product specification. Assume 1 per cent loss to the acetone is acceptable, which will give less than 1 per cent alcohol in the product; fraction in the bottoms 99 per cent,  $\alpha_{541} = 0.99$ .
- Unit 5, Second column. No distillation column can be designed to give complete separation of the components. However, the volatilities for this system are such that a high recovery of alcohol should be practicable. Assume 99 per cent recovery, alcohol recycled,  $\alpha_{151} = 0.99$ .

*Component 2, Acetone ( $k = 2$ )*

- Unit 1. Assume that any acetone in the feed passes through the reactor unchanged,  $\alpha_{212} = 1$ .
- Unit 2. Most of the acetone will condense (b.p. 56°C) say 80 per cent,  $\alpha_{322} = 0.2$ ,  $\alpha_{422} = 0.8$ .
- Unit 3. As for alcohol, assume 99 per cent absorbed, allows for a small loss,  $\alpha_{432} = 0.99$ .
- Unit 4. Assume 99 per cent recovery of acetone as product,  $\alpha_{542} = 0.01$ .
- Unit 5. Because of its high volatility in water all but a few ppm of the acetone will go overhead, put  $\alpha_{152} = 0.01$ .

*Component 3, Hydrogen ( $k = 3$ )*

- Unit 1. Passes through unreacted,  $\alpha_{213} = 1$ .
- Unit 2. Non-condensable,  $\alpha_{323} = 1$ ,  $\alpha_{423} = 0$ .
- Unit 3. None absorbed,  $\alpha_{433} = 0$ .
- Unit 4. Any present in the feed would go out with the overheads,  $\alpha_{543} = 1$ .
- Unit 5. As for unit 4,  $\alpha_{153} = 1$ .

*Component 4, Water ( $k = 4$ )*

- Unit 1. Passes through unreacted,  $\alpha_{214} = 1$ .
- Unit 2. A greater fraction of the water will condense than the alcohol or acetone (b.p. 100°C) assume 95 per cent condensed,  $\alpha_{324} = 0.05$ ,  $\alpha_{423} = 0.95$ .
- Unit 3. There will be a small loss of water in the vent gas stream, assume 1 per cent lost,  $\alpha_{434} = 0.99$ .
- Unit 4. Some water will appear in the acetone product; as for the alcohol this will be fixed by the acetone product specification. Putting  $\alpha_{544} = 0.99$  will give less than 1 per cent water in the product.
- Unit 5. The overhead composition will be close to the azeotropic composition, approximately 9 per cent water. The value of  $\alpha_{154}$  (recycle to the reactor) must be selected

so that the overheads from this unit approximate to the azeotropic composition, as a first try put  $\alpha_{154} = 0.05$ .

### Estimation of fresh feeds

1. Isopropyl alcohol, take the basis of the flow sheet as 100 mol feed,  $g_{101} = 100$ .
2. Acetone formed in the reaction. The overall yield to acetone is approximately 98 per cent, so acetone formed =  $100 \times \frac{98}{2} = 980$  mol,  $g_{202} = 98$  mol.
3. Hydrogen, it is formed in equimolar proportion to acetone, so  $g_{203} = 98$  mol.
4. Water, the feed of water to the scrubber will be dependent on the scrubber design. A typical design value for  $mG_m/L_m$  for a scrubber is 0.7 (see Volume 2, Chapter 4). For the acetone absorption this would require a value of  $L_m$  of 200 mol,  $g_{304} = 200$  mol.

### Matrices

Substituting the values for alcohol ( $k = 1$ ) into the matrix (Figure 4.14) gives the following set of equations for the flow of alcohol into each unit;

$$\begin{bmatrix} 1 & 0 & 0 & 0 & -0.99 \\ -0.1 & 1 & 0 & 0 & 0 \\ 0 & -0.1 & 1 & 0 & 0 \\ 0 & -0.9 & -0.99 & 1 & 0 \\ 0 & 0 & 0 & -0.99 & 1 \end{bmatrix} \times \begin{bmatrix} \lambda_{11} \\ \lambda_{21} \\ \lambda_{31} \\ \lambda_{41} \\ \lambda_{51} \end{bmatrix} = \begin{bmatrix} 100 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Substitution of the values of the split-fraction coefficients for the other components will give the sets of equations for the component flows to each unit. The values of the split-fraction coefficients and fresh feeds are summarised in Table 4.2.

Table 4.2. Split-fraction coefficients and feeds

$\alpha$	$k =$	1	2	3	4
$21k$		-0.1	-1	-1	-1.0
$32k$		-0.1	-0.2	-1	-0.05
$42k$		-0.9	-0.8	0	-0.95
$43k$		-0.99	-0.99	0	-0.99
$54k$		-0.99	-0.01	-1	-0.99
$15k$		-0.99	-0.01	-1	-0.05
		$g_{101}$	$g_{202}$	$g_{203}$	$g_{304}$
Mol		100	98	98	200

### Solution of the equations

The most convenient way to set up and solve the equations is to use a spreadsheet; but any of the standard procedures and programs available for the solution of linear simultaneous equations can be used; Westlake (1968), Mason (1984).

Most proprietary spreadsheets include a routine for the inversion of matrices and the solution of sets of linear simultaneous equations. By using cell references, with cell copying and cell pointing, it is a simple procedure to set up the split fraction matrices

and fresh feed vectors; solve the equations; and use the results to calculate and check the values of any stream composition.

Once the spreadsheet has been set up it is easy to change the values of the split fractions and fresh feeds, and iterate until the design constraints for the problem are satisfied.

The sample problem was solved using an inexpensive, but versatile, spreadsheet package “AS-EASY-AS”<sup>(1)</sup>. The procedure used is illustrated below.

### Procedure

Step 1: Set up the table of split-fractions and fresh feeds, Figure 4.15.

A	.....A/.....	B/.....	C/.....	D/.....	E/.....	F/.....	G/.....	H
1								
2		MASSBAL EXAMPLE USING SPREAD SHEET “AS-EASY-AS”						
3		TO SOLVE EQUATIONS						
4		-----						
5		Split fraction coefficients and fresh feeds						
6		Split fraction coefficients and fresh feeds						
7		Split fraction coefficients and fresh feeds						
8		alpha / k	1	2	3	4		
9								
10		21k	-0.10	-1.00	-1.00	-1.00		
11		32k	-0.10	-0.20	-1.00	-0.05		
12		42k	-0.90	-0.80	0.00	-0.95		
13		43k	-0.99	-0.99	0.00	-0.99		
14		54k	-0.99	-0.01	-1.00	-0.99		
15		15k	-0.99	-0.01	-1.00	-0.05		
16								
17			g101	g202	g203	g304		
18								
19		mol	100.00	98.00	98.00	200.00		
20								

Figure 4.15.

Step 2: Set up an identity matrix of the dimensions needed,  $n \times n$ ; a matrix with 1's on the leading diagonal and 0's elsewhere. For this problem there are 5 units so a  $5 \times 5$  matrix is needed, Figure 4.16.

A	.....A/.....	B/.....	C/.....	D/.....	E/.....	F/.....	G/.....	H	
20									
21		-----							
22		Identity matrix							
23		Identity matrix							
24			1	2	3	4	5	g	Flows
25									
26		1	1.00	0.00	0.00	0.00	0.00	0.00	
27		2	0.00	1.00	0.00	0.00	0.00	0.00	
28		3	0.00	0.00	1.00	0.00	0.00	0.00	
29		4	0.00	0.00	0.00	1.00	0.00	0.00	
30		5	0.00	0.00	0.00	0.00	1.00	0.00	
31									

Figure 4.16.

<sup>(1)</sup> AS-EASY-AS is copyright software developed by TRUIS Inc., North Andover, Massachusetts, USA. Check their web site to download the latest version: [www.truisinc.com](http://www.truisinc.com).

Step 3: Make a copy of the identity matrix, one for each component. For this problem there are 4 components so 4 copies are needed.

Step 4: Copy the appropriate split-fractions and fresh feeds from the table of split-fractions and fresh feeds, Figure 4.15, into the component matrices, Figure 4.17. Copy the cell references, not the actual values. Using the cell references ensures that subsequent changes in the values in the primary table, Figure 4.15, will be copied automatically to the appropriate matrix.

For example, in Figure 4.17 the contents of cell F72 are (F15), not  $-0.05$ .

A ]	.....	A/	.....	B/	.....	C/	.....	D/	.....	E/	.....	F/	.....	G/	.....	H
31																
32																
33																
34																
35																
36																
37																
38																
39	1															
40	2															
41	3															
42	4															
43	5															
44																
45																
46																
47																
48																
49																
50	1															
51	2															
52	3															
53	4															
54	5															
55																
56																
57																
58																
59																
60																
61	1															
62	2															
63	3															
64	4															
65	5															
66																
67																
68																
69																
70																
71																
72	1															
73	2															
74	3															
75	4															
76	5															
77																
78																

Figure 4.17.

Step 5: Use the equation solving routine (E-solve with AS-EASY-AS) to solve the equations and put the results, the flows into each unit, into a column headed “flows”, column H in Figure 4.17; repeat for each component matrix.

Step 6: Transfer (COPY) the component flows into a table and use the SUM function to total the flows in a column, Figure 4.18. Copy the cell references into the table not the values. Examples, from Figure 4.18:

cell C84 contents: (H40)  
 cell C85 contents: (H41)  
 cell G84 contents: SUM(C84..F84)

A ]	.....	A/	.....	B/	.....	C/	.....	D/	.....	E/	.....	F/	.....	G/	.....	H
77																
78																
79																
80																
81																
82																
83																
84																
85																
86																
87																
88																
89																
90																
91																
92																
93																
94																
95																
96																
97																

Figure 4.18.

Step 7: Set up a table to calculate the percentage composition of the stream into each unit; by copying from the table of component flows. The results are shown in Figure 4.18. Example, from Figure 4.18:

cell C92 contents:  $(C83/G83) * 100$

Step 8: Set up the calculations for any values which are design constraints. For example, the overheads, recycle flow, from the second column which should approximate to the azeotropic composition; see Table 4.4. The calculations giving the composition of this stream are shown in Figure 4.19a.

A ]	.....	A/	.....	B/	.....	C/	.....	D/	.....	E/	.....	F/	.....	G/	.....	H
98		<hr/>														
99																
100																
101		Recycle flow composition														
102		alpha 1, 5, 4 = -0.05														
103																
104																
105		Component		1		2		3		4		Total				
106		Flow		10.85		0.01		0.00		10.31		21.17				
107		Percent		51.26		0.05		0.00		48.70						
108		<hr/>														
109																
110																
111																
112		<hr/>														

Figure 4.19a.

A ]	.....	A/	.....	B/	.....	C/	.....	D/	.....	E/	.....	F/	.....	G/	.....	H
98		<hr/>														
99																
100																
101		Recycle flow composition														
102		alpha 1, 5, 4 = -0.0053														
103																
104																
105		Component		1		2		3		4		Total				
106		Flow		10.85		0.01		0.00		1.08		11.94				
107		Per cent		90.88		0.08		0.00		9.04						
108		<hr/>														
109																
110																
111																
112		<hr/>														

Figure 4.19b.

Step 9: Change the values of the appropriate split fractions, or fresh feeds, in the primary table, Figure 4.15, and observe the changes to the calculated values: which will carry through the spread sheet automatically. Iterate on the values until the desired result is obtained.

### **Comments on the first trial solutions**

Table 4.3 shows the feed of each component and the total flow to each unit. The composition of any other stream of interest can be calculated from these values and the split-fraction coefficients. The compositions and flows should be checked for compliance with the process constraints, the split-fraction values adjusted, and the calculation repeated, as necessary, until a satisfactory fit is obtained. Some of the constraints to check in this example are discussed below.



Table 4.3. Solution of equations, feeds to units

Unit	Component	1	2	3	4	Total
1	$\lambda_{1k}$	110.85	0.01	0.0	10.31	121.17
2	$\lambda_{2k}$	11.09	98.01	98.0	10.31	217.41
3	$\lambda_{3k}$	1.11	19.6	98.0	200.51	319.22
4	$\lambda_{4k}$	11.07	97.81	0.0	208.3	317.19
5	$\lambda_{5k}$	10.96	0.98	0.0	206.22	218.16

### **Recycle flow from the second column**

This should approximate to the azeotropic composition (9 per cent alcohol, 91 per cent water). The flow of any component in this stream is given by multiplying the feed to the column ( $\lambda_{5k}$ ) by the split-fraction coefficient for the recycle stream ( $\alpha_{15k}$ ). The calculated flows for each component are shown in Table 4.4.

Table 4.4. Calculation of recycle stream flow

Component	1	2	3	4	Total
$\lambda_{5k}$	10.96	0.98	0.0	206.22	
$\alpha_{15k}$	0.99	0.01	1	0.05	
Flow					21.17
$\alpha_{15k}\lambda_{5k}$	10.85	0.01	0	10.31	
Per cent	51.3	0.05	0	48.7	

Calculated percentage alcohol = 51.3 per cent, required value 91 per cent. Clearly the initial value selected for  $\alpha_{154}$  was too high; too much recycle. Iteration, using the spreadsheet, shows the correct value of  $\alpha_{154}$  to be 0.0053, see Figure 4.19b.

### **Reactor conversion and yield**

$$\begin{aligned} \text{Conversion} &= \frac{\text{alcohol in} - \text{alcohol out}}{\text{alcohol in}} = \frac{\lambda_{11} - \lambda_{21}}{\lambda_{11}} = \frac{110.85 - 11.09}{110.85} \\ &= 90 \text{ per cent, which is the value given} \\ \text{Yield} &= \frac{\text{acetone out}}{\text{alcohol in} - \text{alcohol out}} = \frac{\lambda_{22}}{\lambda_{11} - \lambda_{21}} = \frac{98.01}{110.85 - 11.09} \\ &= 98.3 \text{ per cent, near enough.} \end{aligned}$$

### **Condenser vapour and liquid composition**

The liquid and vapour streams from the partial condenser should be approximately in equilibrium.

The component flows in the vapour stream =  $\alpha_{32k}\lambda_{2k}$  and in the liquid stream =  $\alpha_{42k}\lambda_{2k}$ . The calculation is shown in Table 4.5.

These compositions should be checked against the vapour-liquid equilibrium data for acetone-water and the values of the split-fraction coefficients adjusted, as necessary.

Table 4.5. Condenser vapour and liquid compositions

Component $k$	1	2	3	4	Total
$\lambda_{2k}$	11.09	98.01	98.0	10.31	
$\alpha_{32k}$	0.1	0.2	1	0.05	
Vapour flow					
$\alpha_{32k}\lambda_{2k}$	1.11	19.6	98.0	0.52	119.23
Per cent	0.9	16.4	82.2	0.4	
$\alpha_{42k}$	0.9	0.8	0	0.95	
Liquid flow					
$\alpha_{42k}\lambda_{2k}$	9.98	78.41	0	9.79	98.18
Per cent	10.2	79.9	0	10.0	

### 4.6.3. Guide rules for estimating split-fraction coefficients

The split-fraction coefficients can be estimated by considering the function of the process unit, and by making use of any constraints on the stream flows and compositions that arise from considerations of product quality, safety, phase equilibria, other thermodynamic relationships; and general process and mechanical design considerations. The procedure is similar to the techniques used for the manual calculation of material balances discussed in Section 4.3.

Suggested techniques for use in estimating the split-fraction coefficients for some of the more common unit operations are given below.

#### 1. Reactors

The split-fractions for the reactants can be calculated directly from the percentage conversion. The conversion may be dependent on the relative flows of the reactants (feed composition) and, if so, iteration may be necessary to determine values that satisfy the feed condition.

Conversion is not usually very dependent on the concentration of any inert components.

The pseudo fresh feeds of the products formed in the reactor can be calculated from the specified, or estimated, yields for the process.

#### 2. Mixers

For a unit that simply combines several inlet streams into one outlet stream, the split-fraction coefficients for each component will be equal to 1.  $\alpha_{j,i,k} = 1$ .

#### 3. Stream dividers

If the unit simply divides the inlet stream into two or more outlet streams, each with the same composition as the inlet stream, then the split-fraction coefficient for each component will have the same value as the fractional division of the total stream. A purge stream is an example of this simple division of a process stream into two streams: the main stream and the purge. For example, for a purge rate of 10 per cent the split-fraction coefficients for the purge stream would be 0.1.

#### 4. Absorption or stripping columns

The amount of a component absorbed or stripped in a column is dependent on the column design (the number of stages), the component solubility, and the gas and liquid rates. The fraction absorbed can be estimated using the absorption factor method, attributed to Kremser (1930) (see Volume 2, Chapter 12). If the concentration of solute in the solvent feed to the column is zero, or can be neglected, then for the solute component the fraction absorbed =

$$\frac{(L_m/mG_m)^{s+1} - L_m/mG_m}{(L_m/mG_m)^{s+1} - 1}$$

and for a stripping column, the fraction stripped =

$$\frac{(mG_m/L_m)^{s+1} - (mG_m/L_m)}{(mG_m/L_m)^{s+1} - 1}$$

where  $G_m$  = gas flow rate,  $\text{kmol m}^{-2} \text{ h}^{-1}$ ,  
 $L_m$  = liquid flow rate,  $\text{kmol m}^{-2} \text{ h}^{-1}$ ,  
 $m$  = slope of the equilibrium curve,  
 $s$  = the number of stages.

For a packed column the chart by Colburn (1939) can be used (see Volume 2, Chapter 11). This gives the ratio of the inlet and outlet concentrations,  $y_1/y_2$ , in terms of the number of transfer units and  $mG_m/L_m$ .

The same general approach can be used for solvent extraction processes.

#### 5. Distillation columns

A distillation column divides the feed stream components between the top and bottom streams, and any side streams. The product compositions are often known; they may be specified, or fixed by process constraints, such as product specifications, effluent limits or an azeotropic composition. For a particular stream, “ $s$ ”, the split-fraction coefficient is given by:

$$\frac{x_{sk}r_s}{x_{fk}}$$

where  $x_{sk}$  = the concentration of the component  $k$  in the stream,  $s$ ,  
 $x_{fk}$  = the concentration component  $k$  in the feed stream,  
 $r_s$  = the fraction of the total feed that goes to the stream,  $s$ .

If the feed composition is fixed, or can be estimated, the value of  $r_s$  can be calculated from a mass balance.

The split-fraction coefficients are not very dependent on the feed composition, providing the reflux flow-rate is adjusted so that the ratio of reflux to feed flow is held constant; Vela (1961), Hachmuth (1952).

It is not necessary to specify the reflux when calculating a preliminary material balance; the system boundary can be drawn to include the reflux condenser.

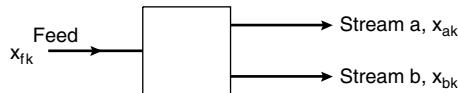
For a column with no side streams the fraction of the total feed flow going to the overheads is given by:

$$r_{\text{overheads}} = \frac{x_{fk} - x_{wk}}{x_{dk} - x_{wk}}$$

where  $x$  is the component composition and the suffixes  $f$ ,  $d$ ,  $w$  refer to feed, overheads and bottoms respectively.

## 6. Equilibrium separators

This is a stream divider with two outlet streams,  $a$  and  $b$ , which may be considered to be in equilibrium.



where  $x_{ak}$  = concentration of component  $k$  in stream  $a$ ,  
 $x_{bk}$  = concentration of component  $k$  in stream  $b$ ,  
 $x_{fk}$  = concentration of component  $k$  in the feed stream.

If the equilibrium relationship can be expressed by a simple equilibrium constant,  $K_k$ , such that:

$$x_{ak} = K_k x_{bk}$$

Then the split-fraction coefficients can be calculated from a material balance.

$$\text{Split fraction for stream } a = \frac{K_k}{K_k - 1} \frac{(x_{fk} - x_{bk})}{x_{fk}}$$

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## 4.8. NOMENCLATURE

	Dimensions in MLT
$G_m$	$\text{ML}^{-2}\text{T}^{-1}$
$g_{iok}$	$\text{MT}^{-1}$
$K_k$	—
$L_m$	$\text{ML}^{-2}\text{T}^{-1}$
$m$	—
$r_s$	—
$s$	—
$x_{ak}$	—
$x_{bk}$	—
$x_{dk}$	—
$x_{fk}$	—
$x_{wk}$	—
$\lambda_{ik}$	$\text{MT}^{-1}$
$\alpha_{jik}$	—

## 4.9. PROBLEMS

**4.1.** Monochlorobenzene is produced by the reaction of benzene with chlorine. A mixture of monochlorobenzene and dichlorobenzene is produced, with a small amount of trichlorobenzene. Hydrogen chloride is produced as a by-product. Benzene is fed to the reactor in excess to promote the production of monochlorobenzene.

The reactor products are fed to a condenser where the chlorobenzenes and unreacted benzene are condensed. The condensate is separated from the non-condensable gases in a separator. The non-condensables, hydrogen chloride and unreacted chlorine, pass to an absorption column where the hydrogen chloride is absorbed in water. The chlorine leaving the absorber is recycled to the reactor.

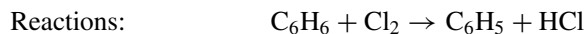
The liquid phase from the separator, chlorobenzenes and unreacted benzene, is fed to a distillation column, where the chlorobenzenes are separated from the unreacted benzene. The benzene is recycled to the reactor.

Using the data given below, calculate the stream flows and draw up a preliminary flow-sheet for the production of 1.0 tonne monochlorobenzene per day.

*Hint:* start the material balance at the reactor inlet (after the addition of the recycle streams) and use a basis of 100 kmol/h benzene at this point.

Data

*Reactor*



mol ratio  $Cl_2 : C_6H_6$  at inlet to reactor = 0.9

overall conversion of benzene = 55.3 per cent

yield of monochlorobenzene = 73.6 per cent

yield of dichlorobenzene = 27.3 per cent

production of other chlorinated compounds can be neglected.

*Condenser*

Assume that all the chlorobenzenes and unreacted benzene condenses. Assume that the vapour pressure of the liquid at the condenser temperature is not significant; i.e. that no chlorobenzene or benzene are carried over in the gas stream.

*Separator*

Assume complete separation of the liquid and gas phases.

*Absorber*

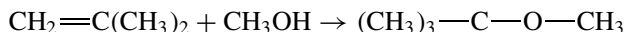
Assume 100 per cent absorption of hydrogen chloride, and that 98 per cent of the chlorine is recycled, the remainder being dissolved in the water. The water supply to the absorber is set to produce a 30 per cent w/w strength hydrochloric acid.

*Distillation column*

Take the recovery of benzene to be 95 per cent, and complete separation of the chlorobenzenes.

- 4.2. Methyl tertiary butyl ether (MTBE) is used as an anti-knock additive in petrol (gasoline).

It is manufactured by the reaction of isobutene with methanol. The reaction is highly selective and practically any  $C_4$  stream containing isobutene can be used as a feedstock



A 10 per cent excess of methanol is used to suppress side reactions.

In a typical process, the conversion of isobutene in the reactor stage is 97 per cent. The product is separated from the unreacted methanol and any  $C_4$ 's by distillation. The essentially pure, liquid, MTBE leaves the base of the distillation column and is sent to storage. The methanol and  $C_4$ 's leave the top of the column as vapour and pass to a column where the methanol is separated by absorption in water. The  $C_4$ 's leave the top of the absorption column, saturated with water, and are used as a fuel gas. The methanol is separated from the water solvent by distillation and recycled to the reactor stage. The water, which leaves the base of the column, is

recycled to the absorption column. A purge is taken from the water recycle stream to prevent the build-up of impurities.

1. Draw up an information flow diagram for this process.
2. Estimate the split fraction coefficients and fresh feeds for each stage.
3. Set up the resulting material balance equations, in matrix form.
4. Solve the equations using a suitable spread-sheet.
5. Adjust the values chosen for the split-fractions and feeds, so the results meet the constraints,
6. Draw a flow-sheet for the process.  
Treat the C<sub>4</sub>'s, other than isobutene, as one component.

Data:

1. Feedstock composition, mol per cent: n-butane = 2, butene-1 = 31, butene-2 = 18, isobutene = 49.
  2. Required production rate of MTBE, 7000 kg/h.
  3. Reactor conversion of isobutene, 97 per cent.
  4. Recovery of MTBE from the distillation column, 99.5 per cent.
  5. Recovery of methanol in the absorption column, 99 per cent.
  6. Concentration of methanol in the solution leaving the absorption column, 15 per cent.
  7. Purge from the water recycle stream, to waste treatment, 10 per cent of the flow leaving the methanol recovery column.
  8. The gases leave the top of the absorption column saturated with water at 30 °C.
  9. Both columns operate at essentially atmospheric pressure.
- 4.3.** Water and ethanol form a low boiling point azeotrope. So, water cannot be completely separated from ethanol by straight distillation. To produce absolute (100 per cent) ethanol it is necessary to add an entraining agent to break the azeotrope. Benzene is an effective entrainer and is used where the product is not required for food products. Three columns are used in the benzene process.
- Column 1.* This column separates the ethanol from the water. The bottom product is essentially pure ethanol. The water in the feed is carried overhead as the ternary azeotrope of ethanol, benzene and water (24 per cent ethanol, 54 per cent benzene, 22 per cent water). The overhead vapour is condensed and the condensate separated in a decanter into, a benzene-rich phase (22 per cent ethanol, 74 per cent benzene, 4 per cent water) and a water-rich phase (35 per cent ethanol, 4 per cent benzene, 61 per cent water). The benzene-rich phase is recycled to the column as reflux. A benzene make-up stream is added to the reflux to make good any loss of benzene from the process. The water-rich phase is fed to the second column.
- Column 2.* This column recovers the benzene as the ternary azeotrope and recycles it as vapour to join the overhead vapour from the first column. The bottom product from the column is essentially free of benzene (29 per cent ethanol, 51 per cent water). This stream is fed to the third column.
- Column 3.* In this column the water is separated and sent to waste treatment. The overhead product consists of the azeotropic mixture of ethanol and water (89 per cent ethanol, 11 per cent water). The overheads are condensed and recycled to join the feed to the first column. The bottom product is essentially free of ethanol.

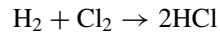
From the compositions given, calculate the stream flows for the production of absolute alcohol from 100 kmol/h raw alcohol feed, composition 89 per cent ethanol, balance water. Take the benzene losses to total 0.1 kmol/h. Draw a preliminary flow-sheet for the process.

All the compositions given are mol percentage.

- 4.4.** A plant is required to produce 10,000 tonnes per year of anhydrous hydrogen chloride from chlorine and hydrogen. The hydrogen source is impure: 90 per cent hydrogen, balance nitrogen.

The chlorine is essentially pure chlorine, supplied in rail tankers.

The hydrogen and chlorine are reacted in a burner at 1.5 bar pressure.



Hydrogen is supplied to the burner in 3 per cent excess over the stoichiometric amount. The conversion of chlorine is essentially 100 per cent. The gases leaving the burner are cooled in a heat exchanger.

The cooled gases pass to an absorption column where the hydrogen chloride gas is absorbed in dilute hydrochloric acid. The absorption column is designed to recover 99.5 per cent of the hydrogen chloride in the feed.

The unreacted hydrogen and inerts pass from the absorber to a vent scrubber where any hydrogen chloride present is neutralised by contact with a dilute, aqueous solution, of sodium hydroxide. The solution is recirculated around the scrubber. The concentration of sodium hydroxide is maintained at 5 per cent by taking a purge from the recycle loop and introducing a make up stream of 25 per cent concentration. The maximum concentration of hydrogen chloride discharged in the gases vented from the scrubber to atmosphere must not exceed 200 ppm (parts per million) by volume.

The strong acid from the absorption column (32 per cent HCl) is fed to a stripping column where the hydrogen chloride gas is recovered from the solution by distillation. The diluted acid from the base of this column (22 per cent HCl), is recycled to the absorption column.

The gases from the top of the stripping column pass through a partial condenser, where the bulk of the water vapour present is condensed and returned to the column as reflux. The gases leaving the column will be saturated with water vapour at 40 °C.

The hydrogen chloride gas leaving the condenser is dried by contact with concentrated sulphuric acid in a packed column. The acid is recirculated over the packing. The concentration of sulphuric acid is maintained at 70 per cent by taking a purge from the recycle loop and introducing a make up stream of strong acid (98 per cent H<sub>2</sub>SO<sub>4</sub>).

The anhydrous hydrogen chloride product is compressed to 5 bar and supplied as a feed to another process.

Using the information provided, calculate the flow-rates and compositions of the main process streams, and draw a flow-sheet for this process.

There is no need to calculate the reflux flow to the distillation column; that will be determined by the column design.



- 4.5. Ammonia is synthesised from hydrogen and nitrogen. The synthesis gas is usually produced from hydrocarbons. The most common raw materials are oil or natural gas; though coal, and even peat can be used.

When produced from natural gas the synthesis gas will be impure, containing up to 5 per cent inerts, mainly methane and argon. The reaction equilibrium and rate are favoured by high pressure. The conversion is low, about 15 per cent and so, after removal of the ammonia produced, the gas is recycled to the converter inlet. A typical process would consist of: a converter (reactor) operating at 350 bar; a refrigerated system to condense out the ammonia product from the recycle loop; and compressors to compress the feed and recycle gas. A purge is taken from the recycle loop to keep the inert concentration in the recycle gas at an acceptable level.

Using the data given below, draw an information flow diagram of the process and calculate the process stream flow-rates and compositions for the production of 600 t/d ammonia. Use either the 'Nagiev' split fraction method, with any suitable spreadsheet; or manual calculations.

Data:

Composition of synthesis gas, mol fraction:

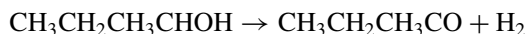
N <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	A
24.5	73.5	1.7	0.3

Temperature and operating pressure of liquid ammonia–gas separator, 340 bar and  $-28^{\circ}\text{C}$ .

Inert gas concentration in recycle gas, not greater than 15 per cent mol per cent.

- 4.6. Methyl ethyl ketone (MEK) is manufactured by the dehydrogenation of 2-butanol. A simplified description of the processes listing the various units used is given below:

1. A reactor in which the butanol is dehydrated to produce MEK and hydrogen, according to the reaction:



The conversion of alcohol to MEK is 88 per cent and the yield can be taken as 100 per cent.

2. A cooler-condenser, in which the reactor off-gases are cooled and most of the MEK and unreacted alcohol are condensed. Two exchangers are used but they can be modelled as one unit. Of the MEK entering the unit 84 per cent is condensed, together with 92 per cent of the alcohol. The hydrogen is non-condensable. The condensate is fed forward to the final purification column.
3. An absorption column, in which the uncondensed MEK and alcohol are absorbed in water.

Around 98 per cent of the MEK and alcohol can be considered to be absorbed in this unit, giving a 10 per cent w/w solution of MEK. The water feed to the absorber is recycled from the next unit, the extractor. The vent stream from the absorber, containing mainly hydrogen, is sent to a flare stack.

4. An extraction column, in which the MEK and alcohol in the solution from the absorber are extracted into trichloroethylene (TCE). The raffinate, water

containing around 0.5 per cent w/w MEK, is recycled to the absorption column. The extract, which contains around 20 per cent w/w MEK, and a small amount of butanol and water, is fed to a distillation column.

5. A distillation column, which separates the MEK and alcohol from the solvent TCE.

The solvent containing a trace of MEK and water is recycled to the extraction column.

6. A second distillation column, which produces a pure MEK product from the crude product from the first column. The residue from this column, which contains the bulk of the unreacted 2-butanol, is recycled to the reactor.

For a production rate of 1250 kg/h MEK:

1. Draw up an information flow diagram for this process.
2. Estimate the split-fraction coefficients and fresh feeds for each stage.
3. Set up the resulting material balance equations, in matrix form.
4. Solve the equations using a suitable spread-sheet.
5. Adjust the values chosen for the split-fractions and feeds, so the results meet the constraints,
6. Draw a flow-sheet for the process.

## CHAPTER 5

# *Piping and Instrumentation*

### 5.1. INTRODUCTION

The process flow-sheet shows the arrangement of the major pieces of equipment and their interconnection. It is a description of the nature of the process.

The Piping and Instrument diagram (P and I diagram or PID) shows the engineering details of the equipment, instruments, piping, valves and fittings; and their arrangement. It is often called the Engineering Flow-sheet or Engineering Line Diagram.

This chapter covers the preparation of the preliminary P and I diagrams at the process design stage of the project.

The design of piping systems, and the specification of the process instrumentation and control systems, is usually done by specialist design groups, and a detailed discussion of piping design and control systems is beyond the scope of this book. Only general guide rules are given. The piping handbook edited by Nayyar *et al.* (2000) is particularly recommended for the guidance on the detailed design of piping systems and process instrumentation and control. The references cited in the text and listed at the end of the chapter should also be consulted.

### 5.2. THE P AND I DIAGRAM

The P and I diagram shows the arrangement of the process equipment, piping, pumps, instruments, valves and other fittings. It should include:

1. All process equipment identified by an equipment number. The equipment should be drawn roughly in proportion, and the location of nozzles shown.
2. All pipes, identified by a line number. The pipe size and material of construction should be shown. The material may be included as part of the line identification number.
3. All valves, control and block valves, with an identification number. The type and size should be shown. The type may be shown by the symbol used for the valve or included in the code used for the valve number.
4. Ancillary fittings that are part of the piping system, such as inline sight-glasses, strainers and steam traps; with an identification number.
5. Pumps, identified by a suitable code number.
6. All control loops and instruments, with an identification number.

For simple processes, the utility (service) lines can be shown on the P and I diagram. For complex processes, separate diagrams should be used to show the service lines, so

the information can be shown clearly, without cluttering up the diagram. The service connections to each unit should, however, be shown on the P and I diagram.

The P and I diagram will resemble the process flow-sheet, but the process information is not shown. The same equipment identification numbers should be used on both diagrams.

### 5.2.1. Symbols and layout

The symbols used to show the equipment, valves, instruments and control loops will depend on the practice of the particular design office. The equipment symbols are usually more detailed than those used for the process flow-sheet. A typical example of a P and I diagram is shown in Figure 5.25.

Standard symbols for instruments, controllers and valves are given in the British Standard BS 1646.

Austin (1979) gives a comprehensive summary of the British Standard symbols, and also shows the American standard symbols (ANSI) and examples of those used by some process plant contracting companies.

The German standard symbols are covered by DIN 28004, DIN (1988).

When laying out the diagram, it is only necessary to show the relative elevation of the process connections to the equipment where these affect the process operation; for example, the net positive suction head (NPSH) of pumps, barometric legs, syphons and the operation of thermosyphon reboilers.

Computer aided drafting programs are available for the preparation of P and I diagrams, see the reference to the PROCEDE package in Chapter 4.

### 5.2.2. Basic symbols

The symbols illustrated below are those given in BS 1646.

#### ***Control valve***

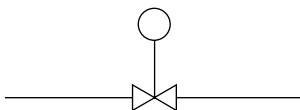


Figure 5.1.

This symbol is used to represent all types of control valve, and both pneumatic and electric actuators.

#### ***Failure mode***

The direction of the arrow shows the position of the valve on failure of the power supply.

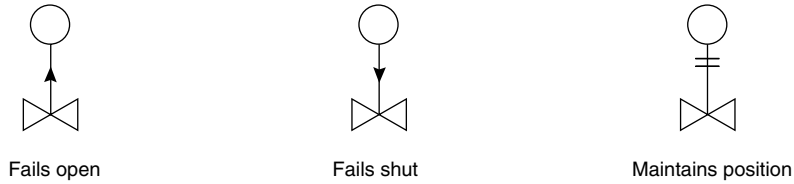


Figure 5.2.

### ***Instruments and controllers***



Figure 5.3.

*Locally mounted* means that the controller and display is located out on the plant near to the sensing instrument location. *Main panel* means that they are located on a panel in the control room. Except on small plants, most controllers would be mounted in the control room.

### ***Type of instrument***

This is indicated on the circle representing the instrument-controller by a letter code (see Table 5.1).

Table 5.1. Letter Code for Instrument Symbols (Based on BS 1646: 1979)

Property measured	First letter	Indicating only	Recording only	Controlling only	Indicating and controlling	Recording and controlling
Flow-rate	F	FI	FR	FC	FIC	FRC
Level	L	LI	LR	LC	LIC	LRC
Pressure	P	PI	PR	PC	PIC	PRC
Quality, analysis	Q	QI	QR	QC	QIC	QRC
Radiation	R	RI	RR	RC	RIC	RRC
Temperature	T	TI	TR	TC	TIC	TRC
Weight	W	WI	WR	WC	WIC	WRC
Any other property (specified in a note)	X	XI	XR	XC	XIC	XRC

Notes:

(1) The letter A may be added to indicate an alarm; with H or L placed next to the instrument circle to indicate high or low.

(2) D is used to show difference or differential; eg. PD for pressure differential.

(3) F, as the second letter indicates ratio; eg. FFC indicates a flow ratio controller.

Consult the standard for the full letter code.

The first letter indicates the property measured; for example, F = flow. Subsequent letters indicate the function; for example,

I = indicating

RC = recorder controller

The suffixes E and A can be added to indicate emergency action and/or alarm functions.

The instrument connecting lines should be drawn in a manner to distinguish them from the main process lines. Dotted or cross-hatched lines are normally used.

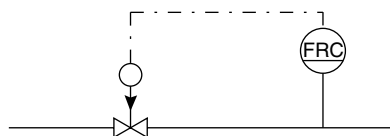


Figure 5.4. A typical control loop

### 5.3. VALVE SELECTION

The valves used for chemical process plant can be divided into two broad classes, depending on their primary function:

1. Shut-off valves (block valves), whose purpose is to close off the flow.
2. Control valves, both manual and automatic, used to regulate flow.

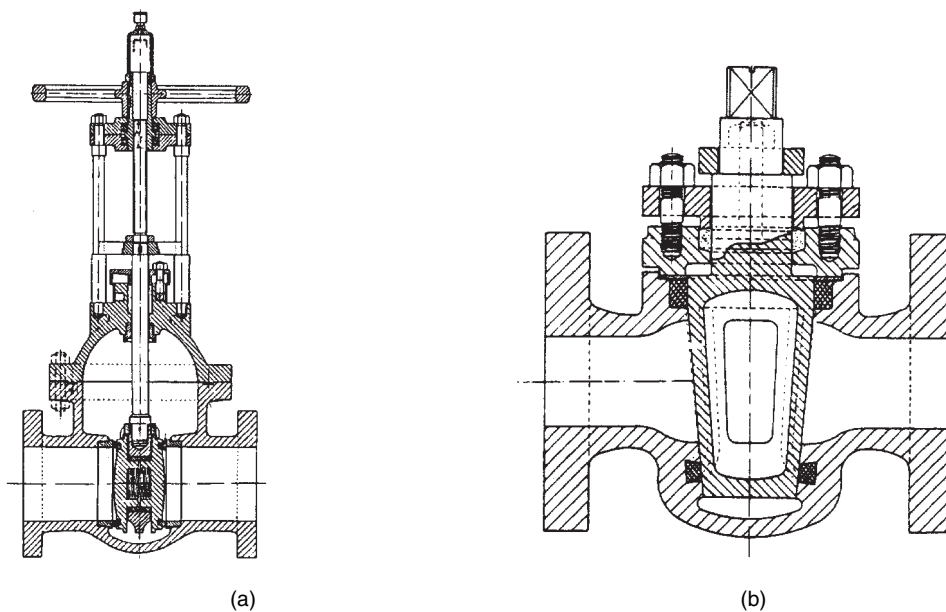
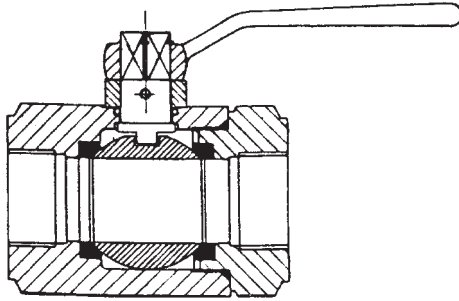
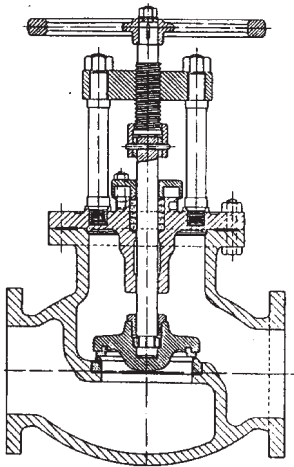


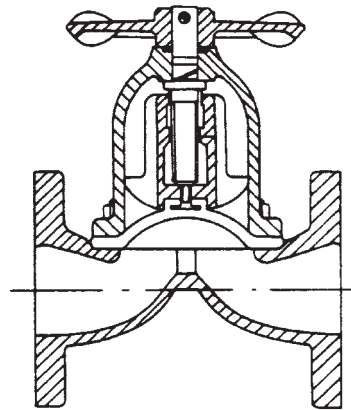
Figure 5.5. (a) Gate valve (slide valve) (b) Plug valve



(c)



(d)



(e)

Figure 5.5. (c) Ball valve (d) Globe valve (e) Diaphragm valve

The main types of valves used are:

Gate	Figure 5.5a
Plug	Figure 5.5b
Ball	Figure 5.5c
Globe	Figure 5.5d
Diaphragm	Figure 5.5e
Butterfly	Figure 5.5f

A valve selected for shut-off purposes should give a positive seal in the closed position and minimum resistance to flow when open. Gate, plug and ball valves are most frequently used for this purpose. The selection of valves is discussed by Merrick (1986) (1990), Smith and Vivian (1995) and Smith and Zappe (2003).

If flow control is required, the valve should be capable of giving smooth control over the full range of flow, from fully open to closed. Globe valves are normally used, though the

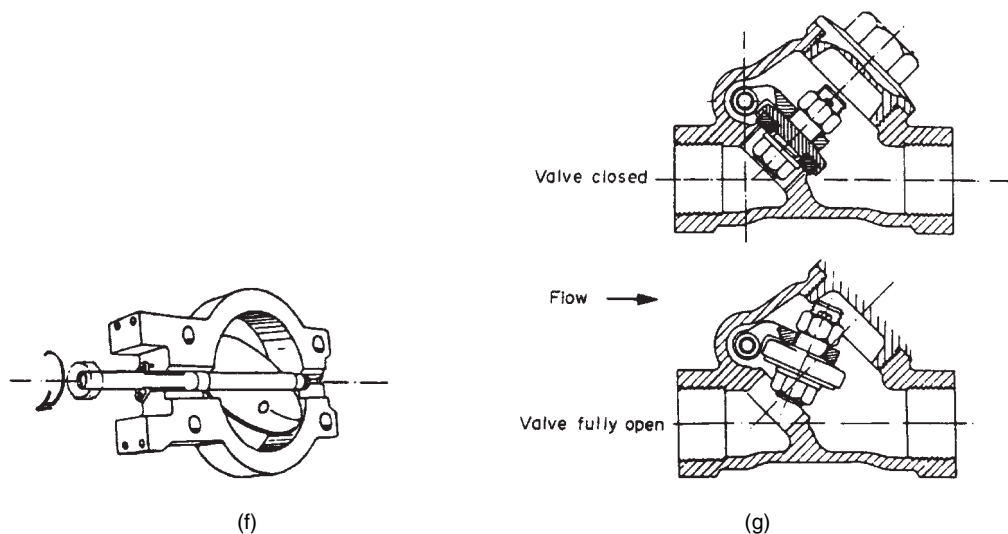


Figure 5.5. (f) Butterfly valve (g) Non-return valve, check valve, hinged disc type

other types can be used. Butterfly valves are often used for the control of gas and vapour flows. Automatic control valves are basically globe valves with special trim designs (see Volume 3, Chapter 7).

The careful selection and design of control valves is important; good flow control must be achieved, whilst keeping the pressure drop as low as possible. The valve must also be sized to avoid the flashing of hot liquids and the super-critical flow of gases and vapours. Control valve sizing is discussed by Chafin (1974).

Non-return valves are used to prevent back-flow of fluid in a process line. They do not normally give an absolute shut-off of the reverse flow. A typical design is shown in Figure 5.5g.

Details of valve types and standards can be found in the technical data manual of the British Valve and Actuators Manufacturers Association, BVAMA (1991). Valve design is covered by Pearson (1978).

## 5.4. PUMPS

### 5.4.1. Pump selection

The pumping of liquids is covered by Volume 1, Chapter 8. Reference should be made to that chapter for a discussion of the principles of pump design and illustrations of the more commonly used pumps.

Pumps can be classified into two general types:

1. Dynamic pumps, such as centrifugal pumps.
2. Positive displacement pumps, such as reciprocating and diaphragm pumps.

The single-stage, horizontal, overhung, centrifugal pump is by far the most commonly used type in the chemical process industry. Other types are used where a high head or other special process considerations are specified.



Pump selection is made on the flow rate and head required, together with other process considerations, such as corrosion or the presence of solids in the fluid.

The chart shown in Figure 5.6 can be used to determine the type of pump required for a particular head and flow rate. This figure is based on one published by Doolin (1977).

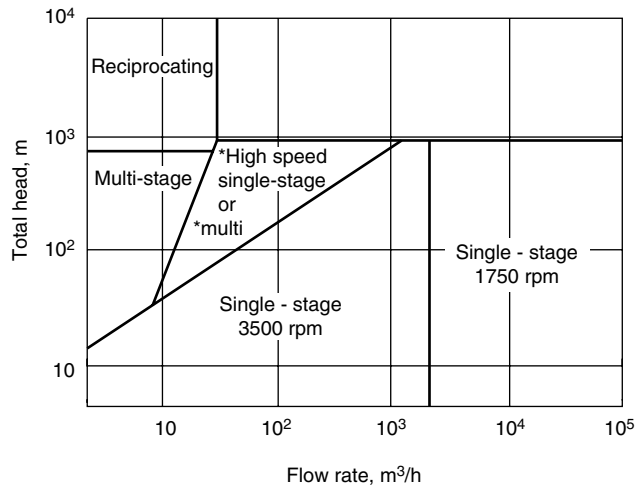


Figure 5.6. Centrifugal pump selection guide. \*Single-stage >1750 rpm, multi-stage 1750 rpm

Centrifugal pumps are characterised by their specific speed (see Volume 1, Chapter 8). In the dimensionless form, specific speed is given by:

$$N_s = \frac{NQ^{1/2}}{(gh)^{3/4}} \quad (5.1)$$

where  $N$  = revolutions per second,

$Q$  = flow, m<sup>3</sup>/s,

$h$  = head, m,

$g$  = gravitational acceleration m/s<sup>2</sup>.

Pump manufacturers do not generally use the dimensionless specific speed, but define it by the equation:

$$N'_s = \frac{NQ'^{1/2}}{h^{3/4}} \quad (5.2)$$

where  $N'_s$  = revolutions per minute (rpm),

$Q'$  = flow, US gal/min,

$h$  = head, ft.

Values of the non-dimensional specific speed, as defined by equation 5.1, can be converted to the form defined by equation 5.2 by multiplying by  $1.73 \times 10^4$ .

The specific speed for centrifugal pumps (equation 5.2) usually lies between 400 and 10,000, depending on the type of impeller. Generally, pump impellers are classified as radial for specific speeds between 400 and 1000, mixed flow between 1500 and 7000, and

axial above 7000. Doolin (1977) states that below a specific speed of 1000 the efficiency of single-stage centrifugal pumps is low and multi-stage pumps should be considered.

For a detailed discussion of the factors governing the selection of the best centrifugal pump for a given duty the reader should refer to the articles by De Santis (1976), Neerkin (1974), Jacobs (1965) or Walas (1983).

Positive displacement, reciprocating, pumps are normally used where a high head is required at a low flow-rate. Holland and Chapman (1966) review the various types of positive displacement pumps available and discuss their applications.

A general guide to the selection, installation and operation of pumps for the processes industries is given by Davidson and von Bertele (1999) and Jandiel (2000).

The selection of the pump cannot be separated from the design of the complete piping system. The total head required will be the sum of the dynamic head due to friction losses in the piping, fittings, valves and process equipment, and any static head due to differences in elevation.

The pressure drop required across a control valve will be a function of the valve design. Sufficient pressure drop must be allowed for when sizing the pump to ensure that the control valve operates satisfactorily over the full range of flow required. If possible, the control valve and pump should be sized together, as a unit, to ensure that the optimum size is selected for both. As a rough guide, if the characteristics are not specified, the control valve pressure drop should be taken as at least 30 per cent of the total dynamic pressure drop through the system, with a minimum value of 50 kPa (7 psi). The valve should be sized for a maximum flow rate 30 per cent above the normal stream flow-rate. Some of the pressure drop across the valve will be recovered downstream, the amount depending on the type of valve used.

Methods for the calculation of pressure drop through pipes and fittings are given in Section 5.4.2 and Volume 1, Chapter 3. It is important that a proper analysis is made of the system and the use of a calculation form (work sheet) to standardize pump-head calculations is recommended. A standard calculation form ensures that a systematic method of calculation is used, and provides a check list to ensure that all the usual factors have been considered. It is also a permanent record of the calculation. Example 5.8 has been set out to illustrate the use of a typical calculation form. The calculation should include a check on the net positive suction head (NPSH) available; see section 5.4.3.

Kern (1975) discusses the practical design of pump suction piping, in a series of articles on the practical aspects of piping system design published in the journal *Chemical Engineering* from December 1973 through to November 1975. A detailed presentation of pipe-sizing techniques is also given by Simpson (1968), who covers liquid, gas and two-phase systems. Line sizing and pump selection is also covered in a comprehensive article by Ludwig (1960).

### 5.4.2. Pressure drop in pipelines

The pressure drop in a pipe, due to friction, is a function of the fluid flow-rate, fluid density and viscosity, pipe diameter, pipe surface roughness and the length of the pipe. It can be calculated using the following equation:

$$\Delta P_f = 8f(L/d_i)\frac{\rho u^2}{2} \quad (5.3)$$

where  $\Delta P_f$  = pressure drop, N/m<sup>2</sup>,  
 $f$  = friction factor,  
 $L$  = pipe length, m,  
 $d_i$  = pipe inside diameter, m,  
 $\rho$  = fluid density, kg/m<sup>3</sup>,  
 $u$  = fluid velocity, m/s.

The friction factor is a dependent on the Reynolds number and pipe roughness. The friction factor for use in equation 5.3 can be found from Figure 5.7.

$$\text{The Reynolds number is given by } Re = (\rho \times u \times d_i) / \mu \quad (5.4)$$

Values for the absolute surface roughness of commonly used pipes are given in Table 5.2. The parameter to use with Figure 5.7 is the relative roughness, given by:

relative roughness,  $e$  = absolute roughness/pipe inside diameter

*Note:* the friction factor used in equation 5.3 is related to the shear stress at the pipe wall,  $R$ , by the equation  $f = (R/\rho u^2)$ . Other workers use different relationships. Their charts for friction factor will give values that are multiples of those given by Figure 5.7. So, it is important to make sure that the pressure drop equation used matches the friction factor chart.

Table 5.2. Pipe roughness

Material	Absolute roughness, mm
Drawn tubing	0.0015
Commercial steel pipe	0.046
Cast iron pipe	0.26
Concrete pipe	0.3 to 3.0

### **Non-Newtonian fluids**

In equation 5.3, and when calculating the Reynolds number for use with Figure 5.7, the fluid viscosity and density are taken to be constant. This will be true for Newtonian liquids but not for non-Newtonian liquids, where the apparent viscosity will be a function of the shear stress.

More complex methods are needed to determine the pressure drop of non-Newtonian fluids in pipelines. Suitable methods are given in Volume 2, Chapter 4, and in Chhabra and Richardson (1999); see also Darby (2001).

### **Gases**

When a gas flows through a pipe the gas density is a function of the pressure and so is determined by the pressure drop. Equation 5.3 and Figure 5.7 can be used to estimate the pressure drop, but it may be necessary to divide the pipeline into short sections and sum the results.

### **Miscellaneous pressure losses**

Any obstruction to flow will generate turbulence and cause a pressure drop. So, pipe fittings, such as: bends, elbows, reducing or enlargement sections, and tee junctions, will increase the pressure drop in a pipeline.

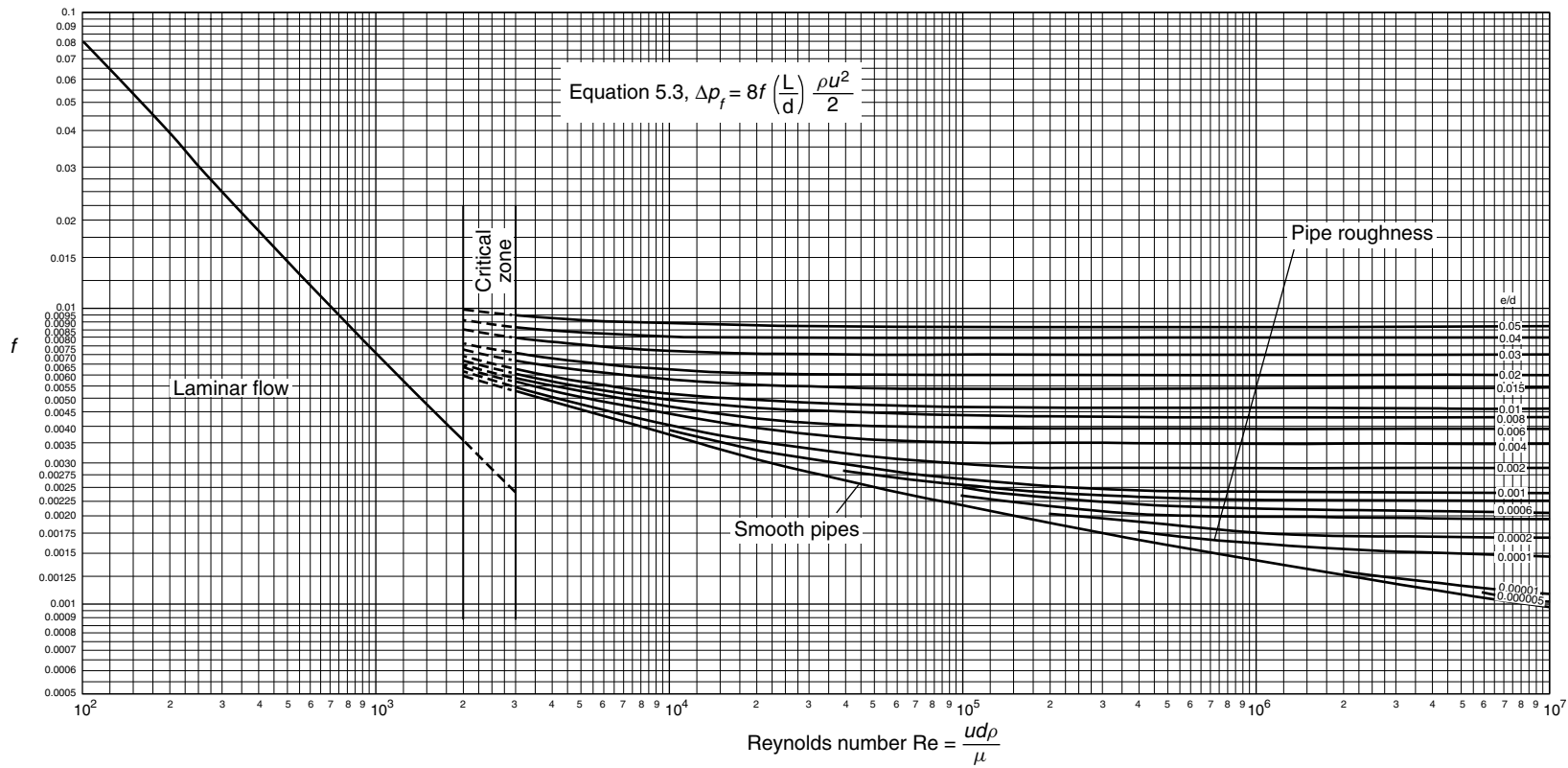


Figure 5.7. Pipe friction versus Reynolds number and relative roughness

There will also be a pressure drop due to the valves used to isolate equipment and control the fluid flow. The pressure drop due to these miscellaneous losses can be estimated using either of two methods:

1. As the number of velocity heads,  $K$ , lost at each fitting or valve.  
A velocity head is  $u^2/2g$ , metres of the fluid, equivalent to  $(u^2/2)\rho$ , N/m<sup>2</sup>. The total number of velocity heads lost due to all the fittings and valves is added to the pressure drop due to pipe friction.
2. As a length of pipe that would cause the same pressure loss as the fitting or valve.  
As this will be a function of the pipe diameter, it is expressed as the number of equivalent pipe diameters. The length of pipe to add to the actual pipe length is found by multiplying the total number of equivalent pipe diameters by the diameter of the pipe being used.

The number of velocity heads lost, or equivalent pipe diameter, is a characteristic of the particular fitting or type of valve used. Values can be found in handbooks and manufacturers' literature. The values for a selected number of fittings and valves are given in Table 5.3.

The two methods used to estimate the miscellaneous losses are illustrated in Example 5.1.

Pipe fittings are discussed in section 5.5.3, see also Perry *et al.* (1997). Valve types and applications are discussed in section 5.3.

Table 5.3. Pressure loss in pipe fittings and valves (for turbulent flow)

Fitting or valve	$K$ , number of velocity heads	number of equivalent pipe diameters
45° standard elbow	0.35	15
45° long radius elbow	0.2	10
90° standard radius elbow	0.6–0.8	30–40
90° standard long elbow	0.45	23
90° square elbow	1.5	75
Tee-entry from leg	1.2	60
Tee-entry into leg	1.8	90
Union and coupling	0.04	2
Sharp reduction (tank outlet)	0.5	25
Sudden expansion (tank inlet)	1.0	50
Gate valve		
fully open	0.15	7.5
1/4 open	16	800
1/2 open	4	200
3/4 open	1	40
Globe valve, bevel seat-		
fully open	6	300
1/2 open	8.5	450
Plug valve - open	0.4	18

### Example 5.1

A pipeline connecting two tanks contains four standard elbows, a plug valve that is fully open and a gate valve that is half open. The line is commercial steel pipe, 25 mm internal diameter, length 120 m.

The properties of the fluid are: viscosity  $0.99 \text{ mNM}^{-2} \text{ s}$ , density  $998 \text{ kg/m}^3$ . Calculate the total pressure drop due to friction when the flow rate is  $3500 \text{ kg/h}$ .

**Solution**

$$\text{Cross-sectional area of pipe} = \frac{\pi}{4}(25 \times 10^{-3})^2 = 0.491 \times 10^{-3} \text{m}^2$$

$$\text{Fluid velocity, } u = \frac{3500}{3600} \times \frac{1}{0.491 \times 10^{-3}} \times \frac{1}{998} = 1.98 \text{ m/s}$$

$$\begin{aligned} \text{Reynolds number, } Re &= (998 \times 1.98 \times 25 \times 10^{-3})/0.99 \times 10^{-3} \\ &= 49,900 = 5 \times 10^4 \end{aligned} \tag{5.4}$$

Absolute roughness commercial steel pipe, Table 5.2 =  $0.046 \text{ mm}$

Relative roughness =  $0.046/(25 \times 10^{-3}) = 0.0018$ , round to  $0.002$

From friction factor chart, Figure 5.7,  $f = 0.0032$

*Miscellaneous losses*

fitting/valve	number of velocity heads, $K$	equivalent pipe diameters
entry	0.5	25
elbows	$(0.8 \times 4)$	$(40 \times 4)$
globe valve, open	6.0	300
gate valve, 1/2 open	4.0	200
exit	<u>1.0</u>	<u>50</u>
Total	14.7	735

*Method 1, velocity heads*

$$\text{A velocity head} = u^2/2g = 1.98^2/(2 \times 9.8) = 0.20 \text{ m of liquid.}$$

$$\text{Head loss} = 0.20 \times 14.7 = 2.94 \text{ m}$$

$$\text{as pressure} = 2.94 \times 998 \times 9.8 = 28,754 \text{ N/m}^2$$

$$\begin{aligned} \text{Friction loss in pipe, } \Delta P_f &= 8 \times 0.0032 \frac{(120)}{(25 \times 10^{-3})} 998 \times \frac{1.98^2}{2} \\ &= 240,388 \text{ N/m}^2 \end{aligned} \tag{5.3}$$

$$\text{Total pressure} = 28,754 + 240,388 = 269,142 \text{ N/m}^2 = \underline{\underline{270 \text{ kN/m}^2}}$$

*Method 2, equivalent pipe diameters*

Extra length of pipe to allow for miscellaneous losses

$$= 735 \times 25 \times 10^{-3} = 18.4 \text{ m}$$

So, total length for  $\Delta P$  calculation =  $120 + 18.4 = 138.4$  m

$$\begin{aligned}\Delta P_f &= 8 \times 0.0032 \frac{(138.4)}{(25 \times 10^{-3})} 998 \times \frac{1.98^2}{2} = 277,247 \text{ N/m}^2 \\ &= \underline{\underline{277 \text{ kN/m}^2}}\end{aligned}\quad (5.3)$$

Note: the two methods will not give exactly the same result. The method using velocity heads is the more fundamentally correct approach, but the use of equivalent diameters is easier to apply and sufficiently accurate for use in design calculations.

### 5.4.3. Power requirements for pumping liquids

To transport a liquid from one vessel to another through a pipeline, energy has to be supplied to:

1. overcome the friction losses in the pipes;
2. overcome the miscellaneous losses in the pipe fittings (e.g. bends), valves, instruments etc.;
3. overcome the losses in process equipment (e.g. heat exchangers);
4. overcome any difference in elevation from end to end of the pipe;
5. overcome any difference in pressure between the vessels at each end of the pipeline.

The total energy required can be calculated from the equation:

$$g\Delta z + \Delta P/\rho - \Delta P_f/\rho - W = 0 \quad (5.5)$$

where  $W$  = work done, J/kg,

$\Delta z$  = difference in elevations ( $z_1 - z_2$ ), m,

$\Delta P$  = difference in system pressures ( $P_1 - P_2$ ), N/m<sup>2</sup>,

$\Delta P_f$  = pressure drop due to friction, including miscellaneous losses, and equipment losses, (see section 5.4.2), N/m<sup>2</sup>,

$\rho$  = liquid density, kg/m<sup>3</sup>,

$g$  = acceleration due to gravity, m/s<sup>2</sup>.

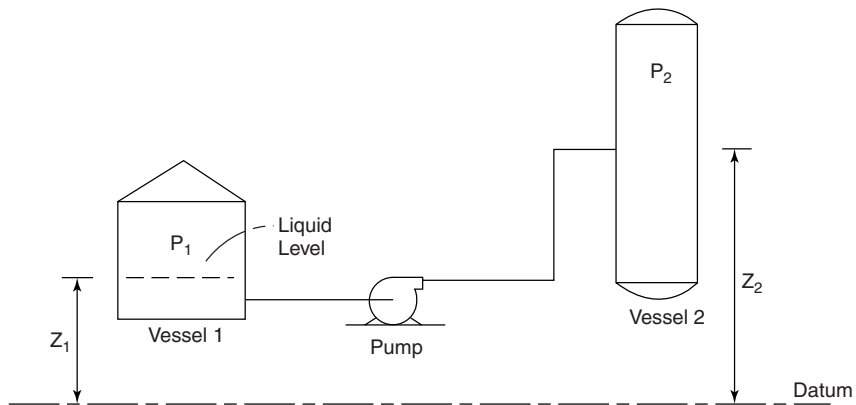


Figure 5.8. Piping system

If  $W$  is negative a pump is required; if it is positive a turbine could be installed to extract energy from the system.

$$\text{The head required from the pump} = \Delta P_f / \rho g - \Delta P / \rho g - \Delta z \tag{5.5a}$$

The power is given by:

$$\text{Power} = (W \times m) / \eta, \text{ for a pump} \tag{5.6a}$$

$$\text{and} = (W \times m) \times \eta, \text{ for a turbine} \tag{5.6b}$$

where  $m$  = mass flow-rate, kg/s,

$\eta$  = efficiency = power out/power in.

The efficiency will depend on the type of pump used and the operating conditions. For preliminary design calculations, the efficiency of centrifugal pumps can be determined using Figure. 5.9.

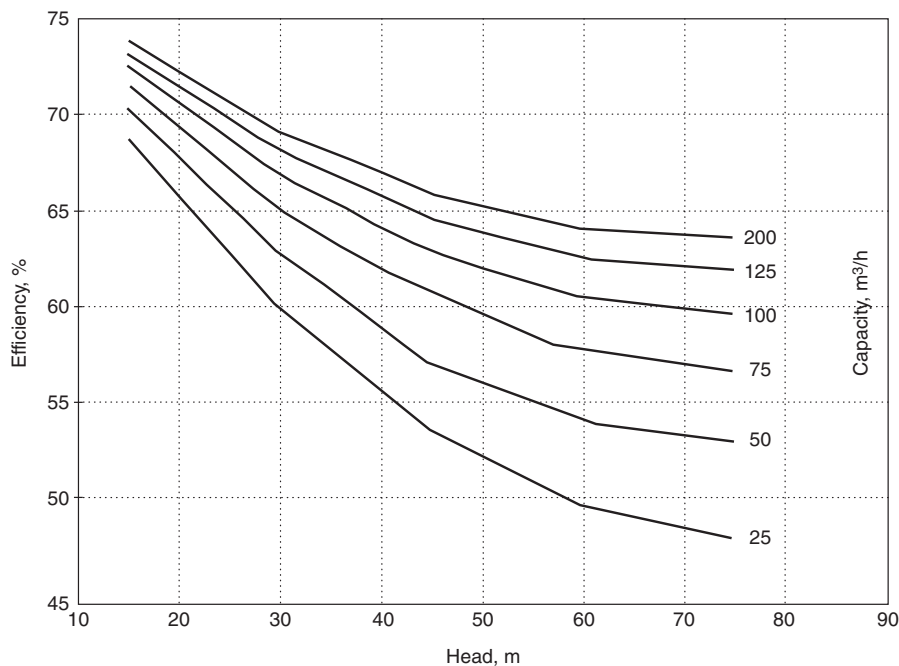


Figure 5.9. Centrifugal pump efficiency

### Example 5.2

A tanker carrying toluene is unloaded, using the ship’s pumps, to an on-shore storage tank. The pipeline is 225 mm internal diameter and 900 m long. Miscellaneous losses due to fittings, valves, etc., amount to 600 equivalent pipe diameters. The maximum liquid level in the storage tank is 30 m above the lowest level in the ship’s tanks. The ship’s



tanks are nitrogen blanketed and maintained at a pressure of 1.05 bar. The storage tank has a floating roof, which exerts a pressure of 1.1 bar on the liquid.

The ship must unload 1000 tonne within 5 hours to avoid demurrage charges. Estimate the power required by the pump. Take the pump efficiency as 70 per cent.

Physical properties of toluene: density  $874 \text{ kg/m}^3$ , viscosity  $0.62 \text{ mNm}^{-2} \text{ s}$ .

### Solution

$$\text{Cross-sectional area of pipe} = \frac{\pi}{4}(225 \times 10^{-3})^2 = 0.0398 \text{ m}^2$$

$$\text{Minimum fluid velocity} = \frac{1000 \times 10^3}{5 \times 3600} \times \frac{1}{0.0398} \times \frac{1}{874} = 1.6 \text{ m/s}$$

$$\begin{aligned} \text{Reynolds number} &= (874 \times 1.6 \times 225 \times 10^{-3}) / 0.62 \times 10^{-3} \\ &= 507,484 = 5.1 \times 10^5 \end{aligned} \quad (5.4)$$

Absolute roughness commercial steel pipe, Table 5.2 = 0.046 mm

Relative roughness =  $0.046/225 = 0.0002$

Friction factor from Figure 5.7,  $f = 0.0019$

Total length of pipeline, including miscellaneous losses,

$$= 900 + 600 \times 225 \times 10^{-3} = 1035 \text{ m}$$

$$\begin{aligned} \text{Friction loss in pipeline, } \Delta P_f &= 8 \times 0.0019 \times \left( \frac{1035}{225 \times 10^{-3}} \right) \times 874 \times \frac{1.6^2}{2} \\ &= \underline{\underline{78,221 \text{ N/m}^2}} \end{aligned} \quad (5.3)$$

Maximum difference in elevation,  $(z_1 - z_2) = (0 - 30) = \underline{\underline{-30 \text{ m}}}$

Pressure difference,  $(P_1 - P_2) = (1.05 - 1.1)10^5 = \underline{\underline{-5 \times 10^3 \text{ N/m}^2}}$

Energy balance

$$9.8(-30) + (-5 \times 103)/874 - (78,221)/874 - W = 0 \quad (5.5)$$

$$W = \underline{\underline{-389.2 \text{ J/kg}}},$$

$$\text{Power} = (389.2 \times 55.56)/0.7 = 30,981 \text{ W, say } \underline{\underline{31 \text{ kW}}}. \quad (5.6a)$$

#### 5.4.4. Characteristic curves for centrifugal pumps

The performance of a centrifugal pump is characterised by plotting the head developed against the flow-rate. The pump efficiency can be shown on the same curve. A typical plot is shown in Figure 5.10. The head developed by the pump falls as the flow-rate is increased. The efficiency rises to a maximum and then falls.

For a given type and design of pump, the performance will depend on the impeller diameter, the pump speed, and the number of stages. Pump manufacturers publish families of operating curves for the range of pumps they sell. These can be used to select the best pump for a given duty. A typical set of curves is shown in Figure 5.11.

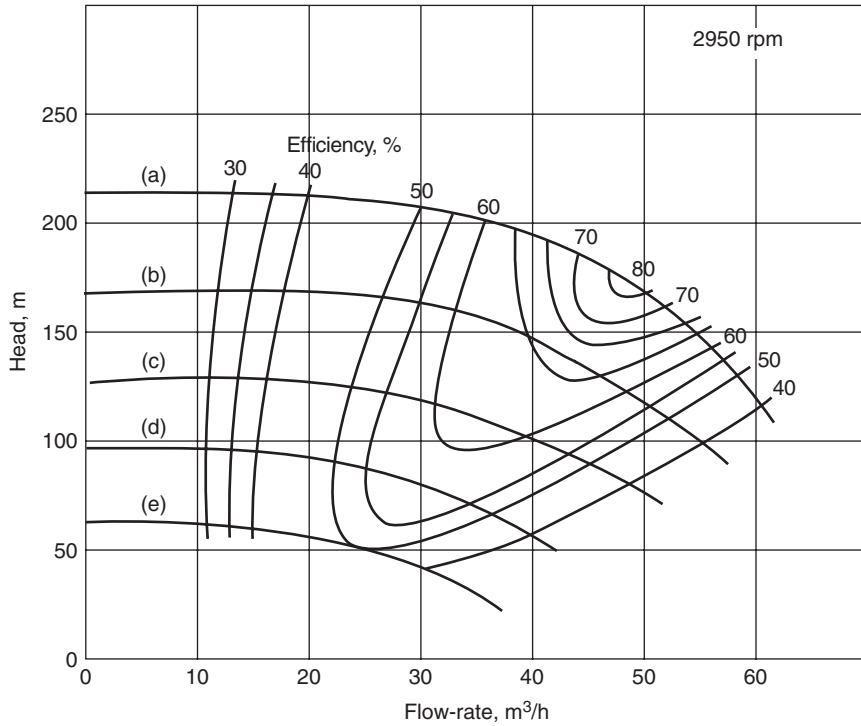


Figure 5.10. Pump characteristic for a range of impeller sizes  
 (a) 250 mm (b) 225 mm (c) 200 (d) 175 mm (e) 150 mm.

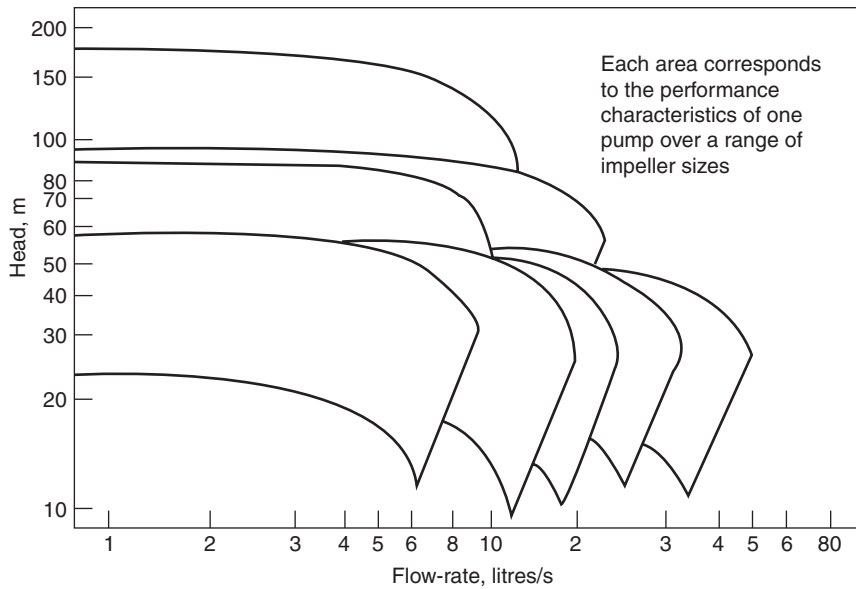


Figure 5.11. Family of pump curves

### 5.4.5. System curve (operating line)

There are two components to the pressure head that has to be supplied by the pump in a piping system:

1. The static pressure, to overcome the differences in head (height) and pressure.
2. The dynamic loss due to friction in the pipe, the miscellaneous losses, and the pressure loss through equipment.

The static pressure difference will be independent of the fluid flow-rate. The dynamic loss will increase as the flow-rate is increased. It will be roughly proportional to the flow-rate squared, see equation 5.3. The system curve, or operating line, is a plot of the total pressure head versus the liquid flow-rate. The operating point of a centrifugal pump can be found by plotting the system curve on the pump's characteristic curve, see Example 5.3.

When selecting a centrifugal pump for a given duty, it is important to match the pump characteristic with system curve. The operating point should be as close as is practical to the point of maximum pump efficiency, allowing for the range of flow-rate over which the pump may be required to operate.

Most centrifugal pumps are controlled by throttling the flow with a valve on the pump discharge, see Section 5.8.3. This varies the dynamic pressure loss, and so the position of the operating point on the pump characteristic curve.

Throttling the flow results in an energy loss, which is acceptable in most applications. However, when the flow-rates are large, the use of variable speed control on the pump drive should be considered to conserve energy.

A more detailed discussion of the operating characteristics of centrifugal and other types of pump is given by Walas (1990) and Karassik *et al.* (2001).

#### Example 5.3

A process liquid is pumped from a storage tank to a distillation column, using a centrifugal pump. The pipeline is 80 mm internal diameter commercial steel pipe, 100 m long. Miscellaneous losses are equivalent to 600 pipe diameters. The storage tank operates at atmospheric pressure and the column at 1.7 bara. The lowest liquid level in the tank will be 1.5 m above the pump inlet, and the feed point to the column is 3 m above the pump inlet.

Plot the system curve on the pump characteristic given in Figure A and determine the operating point and pump efficiency.

Properties of the fluid: density  $900 \text{ kg/m}^3$ , viscosity  $1.36 \text{ mN m}^{-2}\text{s}$ .

#### Solution

##### Static head

$$\text{Difference in elevation, } \Delta z = 3.0 - 1.5 = 1.5 \text{ m}$$

$$\text{Difference in pressure, } \Delta P = (1.7 - 1.013)10^5 = 0.7 \times 10^5 \text{ N/m}^2$$

$$\text{as head of liquid} = (0.7 \times 10^5)/(900 \times 9.8) = 7.9 \text{ m}$$

$$\text{Total static head} = 1.5 + 7.9 = \underline{\underline{9.4 \text{ m}}}$$

**Dynamic head**

As an initial value, take the fluid velocity as 1 m/s, a reasonable value.

$$\text{Cross-sectional area of pipe} = \frac{\pi}{4}(80 \times 10^{-3})^2 = 5.03 \times 10^{-3} \text{ m}^2$$

$$\text{Volumetric flow-rate} = 1 \times 5.03 \times 10^{-3} \times 3600 = 18.1 \text{ m}^3/\text{h}$$

$$\text{Reynolds number} = \frac{900 \times 1 \times 80 \times 10^{-3}}{1.36 \times 10^{-3}} = 5.3 \times 10^4 \quad (5.4)$$

$$\text{Relative roughness} = 0.46/80 = 0.0006$$

Friction factor from Figure 5.7,  $f = 0.0027$

$$\text{Length including miscellaneous losses} = 100 + (600 \times 80 \times 10^3) = 148 \text{ m}$$

$$\begin{aligned} \text{Pressure drop, } \Delta P_f &= 8 \times 0.0027 \frac{(148)}{(80 \times 10^{-3})} \times 900 \times \frac{1^2}{2} = \underline{\underline{17,982 \text{ N/m}^2}} \\ &= 17,982 / (900 \times 9.8) = \underline{\underline{2.03 \text{ m liquid}}} \end{aligned} \quad (5.3)$$

$$\text{Total head} = 9.4 + 2.03 = \underline{\underline{11.4 \text{ m}}}$$

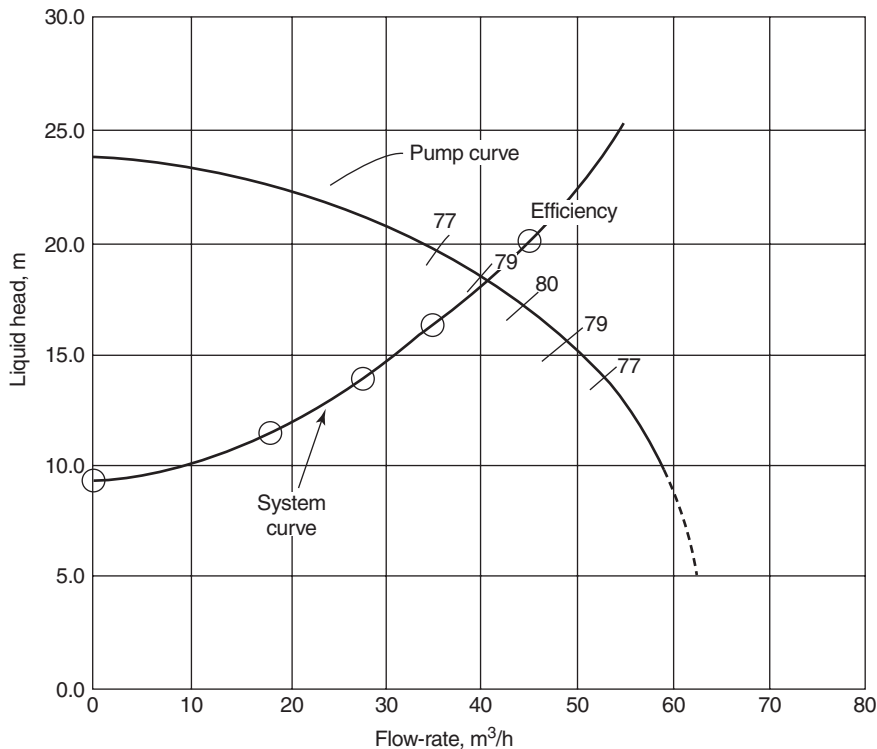


Figure A. Example 5.3

To find the system curve the calculations were repeated for the velocities shown in the table below:

velocity m/s	flow-rate m <sup>3</sup> /h	static head m	dynamic head m	total head m
1	18.1	9.4	2.0	11.4
1.5	27.2	9.4	4.3	14.0
2.0	36.2	9.4	6.8	16.2
2.5	45.3	9.4	10.7	20.1
3.0	54.3	9.4	15.2	24.6

Plotting these values on the pump characteristic gives the operating point as 18.5 m at 40.0 m<sup>3</sup>/h and the pump efficiency as 79 per cent.

#### 5.4.6. Net positive suction head (NPSH)

The pressure at the inlet to a pump must be high enough to prevent cavitation occurring in the pump. Cavitation occurs when bubbles of vapour, or gas, form in the pump casing. Vapour bubbles will form if the pressure falls below the vapour pressure of the liquid.

The net positive suction head available ( $NPSH_{avail}$ ) is the pressure at the pump suction, above the vapour pressure of the liquid, expressed as head of liquid.

The net positive head required ( $NPSH_{reqd}$ ) is a function of the design parameters of the pump, and will be specified by the pump manufacturer. As a general guide, the NPSH should be above 3 m for pump capacities up to 100 m<sup>3</sup>/h, and 6 m above this capacity. Special impeller designs can be used to overcome problems of low suction head; see Doolin (1977).

The net positive head available is given by the following equation:

$$NPSH_{avail} = P/\rho + H - P_f/\rho - P_v/\rho \quad (5.7)$$

where  $NPSH_{avail}$  = net positive suction head available at the pump suction, m,

$P$  = the pressure above the liquid in the feed vessel, N/m<sup>2</sup>,

$H$  = the height of liquid above the pump suction, m,

$P_f$  = the pressure loss in the suction piping, N/m<sup>2</sup>,

$P_v$  = the vapour pressure of the liquid at the pump suction, N/m<sup>2</sup>,

$\rho$  = the density of the liquid at the pump suction temperature, kg/m<sup>3</sup>.

The inlet piping arrangement must be designed to ensure that  $NPSH_{avail}$  exceeds  $NPSH_{reqd}$  under all operating conditions.

The calculation of  $NPSH_{avail}$  is illustrated in Example 5.4.

#### Example 5.4

Liquid chlorine is unloaded from rail tankers into a storage vessel. To provide the necessary NPSH, the transfer pump is placed in a pit below ground level. Given the following information, calculate the NPSH available at the inlet to the pump, at a maximum flow-rate of 16,000 kg/h.

The total length of the pipeline from the rail tanker outlet to the pump inlet is 50 m. The vertical distance from the tank outlet to the pump inlet is 10 m. Commercial steel piping, 50 mm internal diameter, is used.

Miscellaneous friction losses due to the tanker outlet constriction and the pipe fittings in the inlet piping, are equivalent to 1000 equivalent pipe diameters. The vapour pressure of chlorine at the maximum temperature reached at the pump is 685 kN/m<sup>2</sup> and its density and viscosity, 1286 kg/m<sup>3</sup> and 0.364 mNm<sup>-2</sup>s. The pressure in the tanker is 7 bara.

**Solution**

*Friction losses*

$$\begin{aligned}
 \text{Miscellaneous losses} &= 1000 \times 50 \times 10^{-3} = 50 \text{ m of pipe} \\
 \text{Total length of inlet piping} &= 50 + 50 = 100 \text{ m} \\
 \text{Relative roughness, } e/d &= 0.046/50 = 0.001 \\
 \text{Pipe cross-sectional area} &= \frac{\pi}{4} (50 \times 10^{-3})^2 = 1.96 \times 10^{-3} \text{ m}^2 \\
 \text{Velocity, } u &= \frac{16,000}{3600} \times \frac{1}{1.96 \times 10^{-3}} \times \frac{1}{1286} = 1.76 \text{ m/s} \\
 \text{Reynolds number} &= \frac{1286 \times 1.76 \times 50 \times 10^{-3}}{0.364 \times 10^{-3}} = 3.1 \times 10^5 \quad (5.4)
 \end{aligned}$$

Friction factor from Figure 5.7,  $f = 0.00225$

$$\Delta P_f = 8 \times 0.00225 \frac{(100)}{(50 \times 10^{-3})} \times 1286 \times \frac{1.76^2}{2} = 71,703 \text{ N/m}^2 \quad (5.3)$$

$$\begin{aligned}
 \text{NPSH} &= \frac{7 \times 10^5}{1286 \times 9.8} + 10 - \frac{71.703}{1286 \times 9.8} - \frac{685 \times 10^{-3}}{1286 \times 9.8} \\
 &= 55.5 + 10 - 5.7 - 54.4 = \underline{\underline{5.4 \text{ m}}} \quad (5.7)
 \end{aligned}$$

**5.4.7. Pump and other shaft seals**

A seal must be made where a rotating shaft passes through the casing of a pump, or the wall of a vessel. The seal must serve several functions:

1. To keep the liquid contained.
2. To prevent ingress of incompatible fluids, such as air.
3. To prevent escape of flammable or toxic materials.

***Packed glands***

The simplest, and oldest, form of seal is the packed gland, or stuffing box, Figure 5.12. Its applications range from: sealing the stems of the water taps in every home, to proving the seal on industrial pumps, agitator and valve shafts.

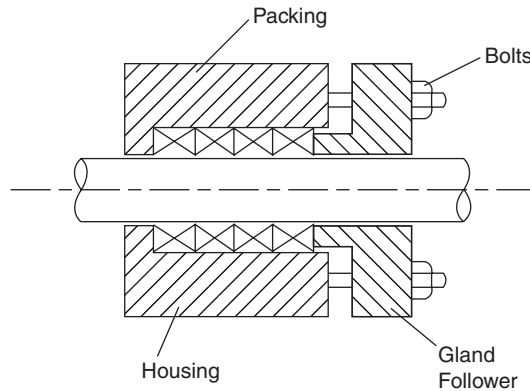


Figure 5.12. Packed gland

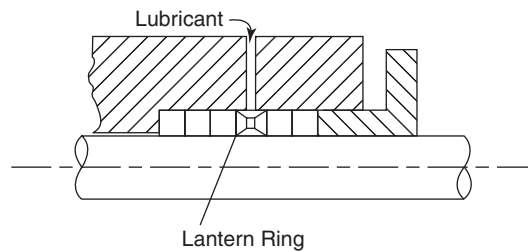


Figure 5.13. Packed gland with lantern ring

The shaft runs through a housing (gland) and the space between the shaft and the wall of the housing is filled with rings of packing. A gland follower is used to apply pressure to the packing to ensure that the seal is tight. Proprietary packing materials are used. A summary of the factors to be considered in the selection of packing materials for packed glands is given by Hoyle (1975). To make a completely tight seal, the pressure on the packing must be 2 to 3 times the system pressure. This can lead to excessive wear on rotating shafts and lower pressures are used; allowing some leakage, which lubricates the packing. So, packed glands should only be specified for fluids that are not toxic, corrosive, or inflammable.

To provide positive lubrication, a lantern ring is often incorporated in the packing and lubricant forced through the ring into the packing, see Figure 5.13. With a pump seal, a flush is often taken from the pump discharge and returned to the seal, through the lantern ring, to lubricate and cool the packing. If any leakage to the environment must be avoided a separate flush liquid can be used. A liquid must be selected that is compatible with the process fluid, and the environment; water is often used.

### ***Mechanical seals***

In the process industries the conditions at the pump seal are often harsh and more complex seals are needed. Mechanical face seals are used, Figure 5.14. They are generally referred to simply as mechanical seals, and are used only on rotating shafts.

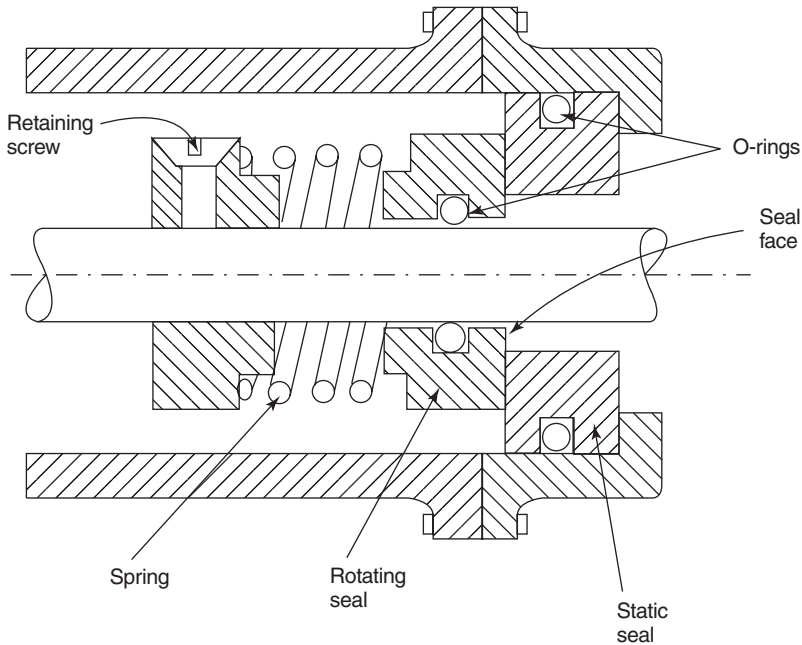


Figure 5.14. Basic mechanical seal

The seal is formed between two flat faces, set perpendicular to the shaft. One face rotates with the shaft, the other is stationary. The seal is made, and the faces lubricated by a very thin film of liquid, about  $0.0001\mu\text{m}$  thick. A particular advantage of this type of seal is that it can provide a very effective seal without causing any wear on the shaft. The wear is transferred to the special seal faces. Some leakage will occur but it is small, normally only a few drops per hour.

Unlike a packed gland, a mechanical seal, when correctly installed and maintained, can be considered leak-tight.

A great variety of mechanical seal designs are available, and seals can be found to suit virtually all applications. Only the basic mechanical seal is described below. Full details, and specifications, of the range of seals available and their applications can be obtained from manufacturers' catalogues.

*The basic mechanical seal*

The components of a mechanical seal, Figure 5.14 are:

1. A stationary sealing ring (mating ring).
2. A seal for the stationary ring, O-rings or gaskets.
3. A rotating seal ring (primary ring), mounted so that it can slide along the shaft to take up wear in the seal faces.
4. A secondary seal for the rotating ring mount; usually O-rings, or or chevron seals.
5. A spring to maintain contact pressure between the seal faces; to push the faces together.



6. A thrust support for the spring; either a collar keyed to the shaft or a step in the shaft.

The assembled seal is fitted into a gland housing (stuffing box) and held in place by a retaining ring (gland plate).

Mechanical seals are classified as inside or outside, depending on whether, the primary (rotating ring) is located inside the housing; running in the fluid, or, outside. Outside seals are easier to maintain, but inside seals are more commonly used in the process industries, as it is easier to lubricate and flush this type.

### *Double seals*

Where it is necessary to prevent any leakage of fluid to the atmosphere, a double mechanical seal is used. The space between the two seals is flushed with a harmless fluid, compatible with the process fluid, and provides a buffer between the two seals.

### **Seal-less pumps (canned pumps)**

Pumps that have no seal on the shaft between the pump and the drive motor are available. They are used for severe duties, where it is essential that there is no leakage into the process fluid, or the environment.

The drive motor and pump are enclosed in a single casing and the stator windings and armature are protected by metal cans; they are usually referred to as canned pumps. The motor runs in the process fluid. The use of canned pumps to control environmental pollution is discussed by Webster (1979).

## **5.5. MECHANICAL DESIGN OF PIPING SYSTEMS**

### **5.5.1. Wall thickness: pipe schedule**

The pipe wall thickness is selected to resist the internal pressure, with an allowance for corrosion. Processes pipes can normally be considered as thin cylinders; only high-pressure pipes, such as high-pressure steam lines, are likely to be classified as thick cylinders and must be given special consideration (see Chapter 13).

The British Standard 5500 gives the following formula for pipe thickness:

$$t = \frac{Pd}{20\sigma_d + P} \quad (5.8)$$

where  $P$  = internal pressure, bar,

$d$  = pipe od, mm,

$\sigma_d$  = design stress at working temperature, N/mm<sup>2</sup>.

Pipes are often specified by a schedule number (based on the thin cylinder formula). The schedule number is defined by:

$$\text{Schedule number} = \frac{P_s \times 1000}{\sigma_s} \quad (5.9)$$

$P_s$  = safe working pressure, lb/in<sup>2</sup> (or N/mm<sup>2</sup>),  
 $\sigma_s$  = safe working stress, lb/in<sup>2</sup> (or N/mm<sup>2</sup>).

Schedule 40 pipe is commonly used for general purposes.

Full details of the preferred dimensions for pipes can be found in the appropriate Handbook and Standards. The main United Kingdom code for pipes and piping systems is the British Standard BS 1600.

The UK pipe schedule numbers are the same as the American (US). A summary of the US standards is given in Perry *et al.* (1997).

### Example 5.5

Estimate the safe working pressure for a 4 in. (100 mm) dia., schedule 40 pipe, carbon steel, butt welded, working temperature 100°C. The safe working stress for butt welded steel pipe up to 120°C is 6000 lb/in<sup>2</sup> (41.4 N/mm<sup>2</sup>).

### Solution

$$P_s = \frac{(\text{schedule no.}) \times \sigma_s}{1000} = \frac{40 \times 6000}{1000} = \underline{\underline{240 \text{ lb/in}^2}} = \underline{\underline{1656 \text{ kN/m}^2}}$$

## 5.5.2. Pipe supports

Over long runs, between buildings and equipment, pipes are usually carried on pipe racks. These carry the main process and service pipes, and are laid out to allow easy access to the equipment.

Various designs of pipe hangers and supports are used to support individual pipes. Details of typical supports can be found in the books by Perry *et al.* (1997) and Holmes (1973). Pipe supports frequently incorporate provision for thermal expansion.

## 5.5.3. Pipe fittings

Pipe runs are normally made up from lengths of pipe, incorporating standard fittings for joints, bends and tees. Joints are usually welded but small sizes may be screwed. Flanged joints are used where this is a more convenient method of assembly, or if the joint will have to be frequently broken for maintenance. Flanged joints are normally used for the final connection to the process equipment, valves and ancillary equipment.

Details of the standard pipe fittings, welded, screwed and flanged, can be found in manufacturer's catalogues and in the appropriate national standards. The standards for metal pipes and fittings are discussed by Masek (1968).

## 5.5.4. Pipe stressing

Piping systems must be designed so as not to impose unacceptable stresses on the equipment to which they are connected.

Loads will arise from:

1. Thermal expansion of the pipes and equipment.
2. The weight of the pipes, their contents, insulation and any ancillary equipment.
3. The reaction to the fluid pressure drop.
4. Loads imposed by the operation of ancillary equipment, such as relief valves.
5. Vibration.

Thermal expansion is a major factor to be considered in the design of piping systems. The reaction load due to pressure drop will normally be negligible. The dead-weight loads can be carried by properly designed supports.

Flexibility is incorporated into piping systems to absorb the thermal expansion. A piping system will have a certain amount of flexibility due to the bends and loops required by the layout. If necessary, expansion loops, bellows and other special expansion devices can be used to take up expansion.

A discussion of the methods used for the calculation of piping flexibility and stress analysis are beyond the scope of this book. Manual calculation techniques, and the application of computers in piping stress analysis, are discussed in the handbook edited by Nayyar *et al.* (2000).

### 5.5.5. Layout and design

An extensive discussion of the techniques used for piping system design and specification is beyond the scope of this book. The subject is covered thoroughly in the books by Sherwood (1991), Kentish (1982a) (1982b), and Lamit (1981).

## 5.6. PIPE SIZE SELECTION

If the motive power to drive the fluid through the pipe is available free, for instance when pressure is let down from one vessel to another or if there is sufficient head for gravity flow, the smallest pipe diameter that gives the required flow-rate would normally be used.

If the fluid has to be pumped through the pipe, the size should be selected to give the least annual operating cost.

Typical pipe velocities and allowable pressure drops, which can be used to estimate pipe sizes, are given below:

	Velocity m/s	$\Delta P$ kPa/m
Liquids, pumped (not viscous)	1–3	0.5
Liquids, gravity flow	—	0.05
Gases and vapours	15–30	0.02 per cent of line pressure
High-pressure steam, >8 bar	30–60	—

Rase (1953) gives expressions for design velocities in terms of the pipe diameter. His expressions, converted to SI units, are:

Pump discharge	$0.06d + 0.4$ m/s
Pump suction	$0.02d + 0.1$ m/s
Steam or vapour	$0.2d$ m/s

where  $d$  is the internal diameter in mm.

Simpson (1968) gives values for the optimum velocity in terms of the fluid density. His values, converted to SI units and rounded, are:

Fluid density $\text{kg/m}^3$	Velocity m/s
1600	2.4
800	3.0
160	4.9
16	9.4
0.16	18.0
0.016	34.0

The maximum velocity should be kept below that at which erosion is likely to occur. For gases and vapours the velocity cannot exceed the critical velocity (sonic velocity) (see Volume 1, Chapter 4) and would normally be limited to 30 per cent of the critical velocity.

### ***Economic pipe diameter***

The capital cost of a pipe run increases with diameter, whereas the pumping costs decrease with increasing diameter. The most economic pipe diameter will be the one which gives the lowest annual operating cost. Several authors have published formulae and nomographs for the estimation of the economic pipe diameter, Genereaux (1937), Peters and Timmerhaus (1968) (1991), Nolte (1978) and Capps (1995). Most apply to American practice and costs, but the method used by Peters and Timmerhaus has been modified to take account of UK prices (Anon, 1971).

The formulae developed in this section are presented as an illustration of a simple optimisation problem in design, and to provide an estimate of economic pipe diameter that is based on UK costs and in SI units. The method used is essentially that first published by Genereaux (1937).

The cost equations can be developed by considering a 1 metre length of pipe.

The purchase cost will be roughly proportional to the diameter raised to some power.

$$\text{Purchase cost} = Bd^n \text{ £/m}$$

The value of the constant  $B$  and the index  $n$  depend on the pipe material and schedule.

The installed cost can be calculated by using the factorial method of costing discussed in Chapter 6.

$$\text{Installed cost} = Bd^n(1 + F)$$

where the factor  $F$  includes the cost of valves, fittings and erection, for a typical run of the pipe.

The capital cost can be included in the operating cost as an annual capital charge. There will also be an annual charge for maintenance, based on the capital cost.

$$Cp = Bd^n(1 + F)(a + b) \tag{5.10}$$

where  $Cp$  = capital cost portion of the annual operating cost, £,  
 $a$  = capital charge, per cent/100,  
 $b$  = maintenance costs, per cent/100.

The power required for pumping is given by:

$$\text{Power} = \text{volumetric flow-rate} \times \text{pressure drop.}$$

Only the friction pressure drop need be considered, as any static head is not a function of the pipe diameter.

To calculate the pressure drop the pipe friction factor needs to be known. This is a function of Reynolds number, which is in turn a function of the pipe diameter. Several expressions have been proposed for relating friction factor to Reynolds number. For simplicity the relationship proposed by Genereaux (1937) for turbulent flow in clean commercial steel pipes will be used.

$$f = 0.04Re^{-0.16}$$

where  $f$  is the Fanning friction factor =  $2(R/\rho u^2)$ .  
 Substituting this into the Fanning pressure drop equation gives:

$$\Delta P = 4.13 \times 10^{10} G^{1.84} \mu^{0.16} \rho^{-1} d^{-4.84} \quad (5.11)$$

where  $\Delta P$  = pressure drop, kN/m<sup>2</sup> (kPa),  
 $G$  = flow rate, kg/s,  
 $\rho$  = density, kg/m<sup>3</sup>,  
 $\mu$  = viscosity, m Nm<sup>-2</sup> s  
 $d$  = pipe id, mm.

The annual pumping costs will be given by:

$$Cf = \frac{Ap}{E} \Delta P \frac{G}{\rho}$$

where  $A$  = plant attainment, hours/year,  
 $p$  = cost of power, £/kWh,  
 $E$  = pump efficiency, per cent/100.

Substituting from equation 5.11

$$Cf = \frac{Hp}{E} 4.13 \times 10^{10} G^{2.84} \mu^{0.16} \rho^{-2} d^{-4.84} \quad (5.12)$$

The total annual operating cost  $Ct = Cp + Cf$ .

Adding equations 5.10 and 5.12, differentiating, and equating to zero to find the pipe diameter to give the minimum cost gives:

$$d, \text{ optimum} = \left[ \frac{2 \times 10^{11} \times ApG^{2.84} \mu^{0.16} \rho^{-2}}{EnB(1+F)(a+b)} \right]^{1/(4.84+n)} \quad (5.13)$$

Equation 5.13 is a general equation and can be used to estimate the economic pipe diameter for any particular situation. It can be set up on a spreadsheet and the effect of the various factors investigated.

The equation can be simplified by substituting typical values for the constants.

- A* The normal attainment for a chemical process plant will be between 90–95%, so take the operating hours per year as 8000.
- E* Pump and compressor efficiencies will be between 50 to 70%, so take 0.6.
- p* Use the current cost of power, 0.055 £/kWh (mid-1992).
- F* This is the most difficult factor to estimate. Other authors have used values ranging from 1.5 (Peters and Timmerhaus (1968)) to 6.75 (Nolte (1978)). It is best taken as a function of the pipe diameter; as has been done to derive the simplified equations given below.
- B, n* Can be estimated from the current cost of piping.
- a* Will depend on the current cost of capital, around 10% in mid-1992.
- b* A typical figure for process plant will be 5%, see Chapter 6.

*F, B,* and *n* have been estimated from cost data published by the Institution of Chemical Engineers, IChemE (1987), updated to mid-1992. This includes the cost of fittings, installation and testing. A log-log plot of the data gives the following expressions for the installed cost:

$$\begin{array}{ll} \text{Carbon steel, 15 to 350 mm} & 27 d^{0.55} \text{ £/m} \\ \text{Stainless steel, 15 to 350 mm} & 31 d^{0.62} \text{ £/m} \end{array}$$

Substitution in equation 5.12 gives, for carbon steel:

$$d, \text{ optimum} = 366 G^{0.53} \mu^{0.03} \rho^{-0.37}$$

Because the exponent of the viscosity term is small, its value will change very little over a wide range of viscosity

$$\begin{array}{l} \text{at} \\ \mu = 10^{-5} \text{ Nm}^{-2}\text{s (0.01 cp), } \mu^{0.03} = 0.71 \\ \mu = 10^{-2} \text{ Nm}^{-2}\text{s (10 cp), } \mu^{0.03} = 0.88 \end{array}$$

Taking a mean value of 0.8, gives the following equations for the optimum diameter, for turbulent flow:

Carbon steel pipe:

$$d, \text{ optimum} = 293 G^{0.53} \rho^{-0.37} \quad (5.14)$$

Stainless steel pipe:

$$d, \text{ optimum} = 260 G^{0.52} \rho^{-0.37} \quad (5.15)$$

Equations 5.14 and 5.15 can be used to make an approximate estimate of the economic pipe diameter for normal pipe runs. For a more accurate estimate, or if the fluid or pipe run is unusual, the method used to develop equation 5.13 can be used, taking into account the special features of the particular pipe run.

The optimum diameter obtained from equations 5.14 and 5.15 should remain valid with time. The cost of piping depends on the cost power and the two costs appear in the equation as a ratio raised to a small fractional exponent.

Equations for the optimum pipe diameter with laminar flow can be developed by using a suitable equation for pressure drop in the equation for pumping costs.

The approximate equations should not be used for steam, as the quality of steam depends on its pressure, and hence the pressure drop.

Nolte (1978) gives detailed methods for the selection of economic pipe diameters, taking into account all the factors involved. He gives equations for liquids, gases, steam and two-phase systems. He includes in his method an allowance for the pressure drop due to fittings and valves, which was neglected in the development of equation 5.12, and by most other authors.

The use of equations 5.14 and 5.15 are illustrated in Examples 5.6 and 5.7, and the results compared with those obtained by other authors. Peters and Timmerhaus's formulae give larger values for the economic pipe diameters, which is probably due to their low value for the installation cost factor,  $F$ .

### Example 5.6

Estimate the optimum pipe diameter for a water flow rate of 10 kg/s, at 20°C. Carbon steel pipe will be used. Density of water 1000 kg/m<sup>3</sup>.

#### Solution

$$\begin{aligned} d, \text{ optimum} &= 293 \times (10)^{0.53} 1000^{-0.37} \\ &= \underline{\underline{77.1 \text{ mm}}} \end{aligned} \quad (5.14)$$

use 80-mm pipe.

Viscosity of water at 20°C =  $1.1 \times 10^{-3}$  Ns/m<sup>2</sup>,

$$Re = \frac{4G}{\pi\mu d} = \frac{4 \times 10}{\pi \times 1.1 \times 10^{-3} \times 80 \times 10^{-3}} = 1.45 \times 10^5$$

>4000, so flow is turbulent.

Comparison of methods:

	Economic diameter
Equation 5.14	180 mm
Peters and Timmerhaus (1991)	4 in. (100 mm)
Nolte (1978)	80 mm

### Example 5.7

Estimate the optimum pipe diameter for a flow of HCl of 7000 kg/h at 5 bar, 15°C, stainless steel pipe. Molar volume 22.4 m<sup>3</sup>/kmol, at 1 bar, 0°C.

#### Solution

Molecular weight HCl = 36.5.

$$\text{Density at operating conditions} = \frac{36.5}{22.4} \times \frac{5}{1} \times \frac{273}{288} = \underline{\underline{7.72 \text{ kg/m}^3}}$$

$$\begin{aligned} \text{Optimum diameter} &= 260 \left( \frac{7000}{3600} \right)^{0.52} 7.72^{-0.37} \\ &= \underline{\underline{172.4 \text{ mm}}} \end{aligned} \tag{5.15}$$

use 180-mm pipe.

Viscosity of HCl 0.013 m Ns/m<sup>2</sup>

$$Re = \frac{4}{\pi} \times \frac{7000}{3600} \times \frac{1}{0.013 \times 10^{-3} \times 180 \times 10^{-3}} = \underline{\underline{1.06 \times 10^6}}, \text{ turbulent}$$

Comparison of methods:

	Economic diameter
Equation 5.15	180 mm
Peters and Timmerhaus (1991)	9 in. (220 mm) carbon steel
Nolte (1978)	7 in. (180 mm) carbon steel

**Example 5.8**

Calculate the line size and specify the pump required for the line shown in Figure 5.15; material ortho-dichlorobenzene (ODCB), flow-rate 10,000 kg/h, temperature 20°C, pipe material carbon steel.

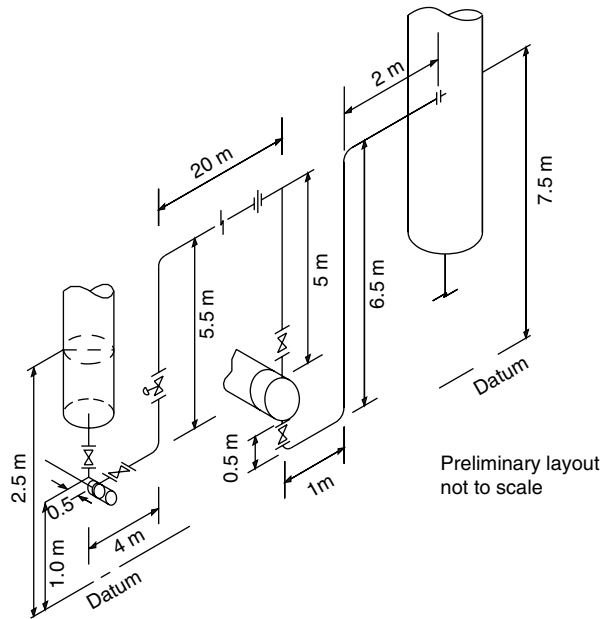


Figure 5.15. Piping isometric drawing (Example 5.8)



**Solution**

ODCB density at 20°C = 1306 kg/m<sup>3</sup>.

Viscosity: 0.9 mNs/m<sup>2</sup> (0.9 cp).

*Estimation of pipe diameter required*

typical velocity for liquid 2 m/s

$$\text{mass flow} = \frac{10,000}{3600} = 2.78 \text{ kg/s}$$

$$\text{volumetric flow} = \frac{2.78}{1306} = 2.13 \times 10^{-3} \text{ m}^3/\text{s}$$

$$\text{area of pipe} = \frac{\text{volumetric flow}}{\text{velocity}} = \frac{2.13 \times 10^{-3}}{2} = 1.06 \times 10^{-3} \text{ m}^2$$

$$\begin{aligned} \text{diameter of pipe} &= \sqrt{\left(1.06 \times 10^{-3} \times \frac{4}{\pi}\right)} = 0.037 \text{ m} \\ &= 37 \text{ mm} \end{aligned}$$

Or, use economic pipe diameter formula:

$$\begin{aligned} d, \text{ optimum} &= 293 \times 2.78^{0.53} \times 1306^{-0.37} \\ &= 35.4 \text{ mm} \end{aligned} \quad (5.14)$$

Take diameter as 40 mm

$$\text{cross-sectional area} = \frac{\pi}{4}(40 \times 10^{-3})^2 = 1.26 \times 10^{-3} \text{ m}^2$$

*Pressure drop calculation*

$$\text{fluid velocity} = \frac{2.13 \times 10^{-3}}{1.26 \times 10^{-3}} = 1.70 \text{ m/s}$$

Friction loss per unit length,  $\Delta f_1$ :

$$Re = \frac{1306 \times 1.70 \times 40 \times 10^{-3}}{0.9 \times 10^{-3}} = 9.9 \times 10^4 \quad (5.5)$$

Absolute roughness commercial steel pipe, table 5.2 = 0.46 mm

Relative roughness,  $e/d = 0.046/40 = 0.001$

Friction factor from Figure 5.7,  $f = 0.0027$

$$\begin{aligned} \Delta f_1 &= 8 \times 0.0027 \times \frac{(1)}{(40 \times 10^{-3})} \times 1306 \times \frac{1.7^2}{2} = 1019 \text{ N/m}^2 \\ &= 1.02 \text{ kPa} \end{aligned} \quad (5.3)$$

Design for a maximum flow-rate of 20 per cent above the average flow.

$$\text{Friction loss} = 1.02 \times 1.2^2 = 1.5 \text{ kPa/m}$$

*Miscellaneous losses*

Take as equivalent pipe diameters. All bends will be taken as 90° standard radius elbow.

Line to pump suction:

length	=	1.5 m
bend, $1 \times 30 \times 40 \times 10^{-3}$	=	1.2 m
valve, $1 \times 18 \times 40 \times 10^{-3}$	=	0.7 m
		3.4 m

$$\text{entry loss} = \frac{\rho u^2}{2} \text{ (see Section 5.4.2)}$$

$$\text{at maximum design velocity} = \frac{1306(1.7 \times 1.2)^2}{2 \times 10^3} = 2.7 \text{ kPa}$$

Control valve pressure drop, allow normal	140 kPa
( $\times 1.2^2$ ) maximum	200 kPa
Heat exchanger, allow normal	70 kPa
( $\times 1.2^2$ ) maximum	100 kPa
Orifice, allow normal	15 kPa
( $\times 1.2^2$ ) maximum	22 kPa

Line from pump discharge:

length = $4 + 5.5 + 20 + 5 + 0.5 + 1 + 6.5 + 2$	=	44.5 m
bends, $6 \times 30 \times 40 \times 10^{-3}$	=	7.2 m
valves, $3 \times 18 \times 40 \times 10^{-3}$	=	2.2 m
		54.0 m

The line pressure-drop calculation is set out on the calculation sheet shown in Table 5.4.

Pump selection:

flow-rate =  $2.13 \times 10^{-3} \times 3600 = 7.7 \text{ m}^3/\text{h}$   
 differential head, maximum, 44 m  
 select single-stage centrifugal (Figure 5.6)

Table 5.4. Line calculation form (Example 5.4)

Pump and line calculation sheet									
Job no.	Sheet no.	By RKS, 7/7/79			Checked				
4415A	1								
Fluid	ODCB			DISCHARGE CALCULATION					
Temperature °C	20			Line size mm		40			
Density kg/m <sup>3</sup>	1306			Flow	Norm.	Max.	Units		
Viscosity mNs/m <sup>2</sup>	0.9			u <sub>2</sub>	Velocity	1.7	2.0	m/s	
Normal flow kg/s	2.78			Δf <sub>2</sub>	Friction loss	1.0	1.5	kPa/m	
Design max. flow kg/s	3.34			L <sub>2</sub>	Line length	54	—	m	
				Δf <sub>2</sub> L <sub>2</sub>	Line loss	54		kPa	
SUCTION CALCULATION									
Line size mm		40		30%	Control valve	140	200	kPa	
	Flow	Norm.	Max.	Units	Equipment				
u <sub>1</sub>	Velocity	1.7	2.0	m/s	(a) Heat ex.	70	100	kPa	
Δf <sub>1</sub>	Friction loss	1.0	1.5	kPa/m	(b)	—	—	kPa	
L <sub>1</sub>	Line length	3.4	—	m	(c)	—	—	kPa	
Δf <sub>1</sub> L <sub>1</sub>	Line loss	3.4	5.1	kPa	(6) Dynamic loss	279	403	kPa	
ρu <sub>1</sub> <sup>2</sup> /2	Entrance	1.9	2.7	kPa	z <sub>2</sub>	Static head	6.5	—	m
(40 kPa)	Strainer	—	—	kPa					
	(1) Sub-total	5.3	7.8	kPa		Equip. press (max)	200	200	kPa
z <sub>1</sub>	Static head	1.5	1.5	m		Contingency	None	None	kPa
ρgz <sub>1</sub>		19.6	19.6	kPa		(7) Sub-total	285	285	kPa
	Equip. press	100	100	kPa	(7) + (6)	Discharge press.	564	685	kPa
	(2) Sub-total	119.6	119.6	kPa	(3)	Suction press.	114.3	111.8	kPa
(2) - (1)	(3) Suction press	114.3	111.8	kPa	(8)/ρg	(8) Diff. press.	450	576	kPa
	(4) VAP. PRESS.	0.1	0.1	kPa					
(3) - (4)	(5) NPSH	114.2	111.7	kPa	Valve/(6)	Control valve % Dyn. loss	50%		
(5)/ρg		8.7	8.6	m					

$Z_1 = 2.5 - 1 = 1.5 \text{ m}$   
 $Z_2 = 7.5 - 1 = 6.5 \text{ m}$

Table 5.5. Pump Specification Sheet (Example 5.8)

<i>Pump Specification</i>	
Type:	Centrifugal
No. stages:	1
Single/Double suction:	Single
Vertical/Horizontal mounting:	Horizontal
Impeller type:	Closed
Casing design press.:	600 kPa
design temp.:	20°C
Driver:	Electric, 440 V, 50 c/s 3-phase.
Seal type:	Mechanical, external flush
Max. flow:	7.7 m <sup>3</sup> /h
Diff. press.:	600 kPa (47 m, water)

## 5.7. CONTROL AND INSTRUMENTATION

### 5.7.1. Instruments

Instruments are provided to monitor the key process variables during plant operation. They may be incorporated in automatic control loops, or used for the manual monitoring of the process operation. They may also be part of an automatic computer data logging system. Instruments monitoring critical process variables will be fitted with automatic alarms to alert the operators to critical and hazardous situations.

Comprehensive reviews of process instruments and control equipment are published periodically in the journal *Chemical Engineering*. These reviews give details of all the instruments and control hardware available commercially, including those for the on-line analysis of stream compositions (Anon., 1969). Details of process instruments and control equipment can also be found in various handbooks, Perry *et al.* (1997) and Lipak (2003).

It is desirable that the process variable to be monitored be measured directly; often, however, this is impractical and some dependent variable, that is easier to measure, is monitored in its place. For example, in the control of distillation columns the continuous, on-line, analysis of the overhead product is desirable but difficult and expensive to achieve reliably, so temperature is often monitored as an indication of composition. The temperature instrument may form part of a control loop controlling, say, reflux flow; with the composition of the overheads checked frequently by sampling and laboratory analysis.

### 5.7.2. Instrumentation and control objectives

The primary objectives of the designer when specifying instrumentation and control schemes are:

1. Safe plant operation:
  - (a) To keep the process variables within known safe operating limits.
  - (b) To detect dangerous situations as they develop and to provide alarms and automatic shut-down systems.
  - (c) To provide interlocks and alarms to prevent dangerous operating procedures.
2. Production rate:
 

To achieve the design product output.

3. Product quality:  
To maintain the product composition within the specified quality standards.
4. Cost:  
To operate at the lowest production cost, commensurate with the other objectives.

These are not separate objectives and must be considered together. The order in which they are listed is not meant to imply the precedence of any objective over another, other than that of putting safety first. Product quality, production rate and the cost of production will be dependent on sales requirements. For example, it may be a better strategy to produce a better-quality product at a higher cost.

In a typical chemical processing plant these objectives are achieved by a combination of automatic control, manual monitoring and laboratory analysis.

### 5.7.3. Automatic-control schemes

The detailed design and specification of the automatic control schemes for a large project is usually done by specialists. The basic theory underlying the design and specification of automatic control systems is covered in several texts: Coughanowr (1991), Shinskey (1984) (1996) and Perry *et al.* (1997). The books by Murrill (1988) and Shinskey (1996) cover many of the more practical aspects of process control system design, and are recommended.

In this chapter only the first step in the specification of the control systems for a process will be considered: the preparation of a preliminary scheme of instrumentation and control, developed from the process flow-sheet. This can be drawn up by the process designer based on his experience with similar plant and his critical assessment of the process requirements. Many of the control loops will be conventional and a detailed analysis of the system behaviour will not be needed, nor justified. Judgement, based on experience, must be used to decide which systems are critical and need detailed analysis and design.

Some examples of typical (conventional) control systems used for the control of specific process variables and unit operations are given in the next section, and can be used as a guide in preparing preliminary instrumentation and control schemes.

#### **Guide rules**

The following procedure can be used when drawing up preliminary P and I diagrams:

1. Identify and draw in those control loops that are obviously needed for steady plant operation, such as:
  - (a) level controls,
  - (b) flow controls,
  - (c) pressure controls,
  - (d) temperature controls.
2. Identify the key process variables that need to be controlled to achieve the specified product quality. Include control loops using direct measurement of the controlled variable, where possible; if not practicable, select a suitable dependent variable.
3. Identify and include those additional control loops required for safe operation, not already covered in steps 1 and 2.

4. Decide and show those ancillary instruments needed for the monitoring of the plant operation by the operators; and for trouble-shooting and plant development. It is well worthwhile including additional connections for instruments which may be needed for future trouble-shooting and development, even if the instruments are not installed permanently. This would include: extra thermowells, pressure tappings, orifice flanges, and extra sample points.
5. Decide on the location of sample points.
6. Decide on the need for recorders and the location of the readout points, local or control room. This step would be done in conjunction with steps 1 to 4.
7. Decide on the alarms and interlocks needed; this would be done in conjunction with step 3 (see Chapter 9).

## 5.8. TYPICAL CONTROL SYSTEMS

### 5.8.1. Level control

In any equipment where an interface exists between two phases (e.g. liquid–vapour), some means of maintaining the interface at the required level must be provided. This may be incorporated in the design of the equipment, as is usually done for decanters, or by automatic control of the flow from the equipment. Figure 5.16 shows a typical arrangement for the level control at the base of a column. The control valve should be placed on the discharge line from the pump.

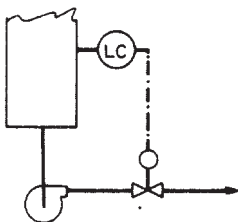


Figure 5.16. Level control

### 5.8.2. Pressure control

Pressure control will be necessary for most systems handling vapour or gas. The method of control will depend on the nature of the process. Typical schemes are shown in Figures 5.17*a, b, c, d* (see p. 230). The scheme shown in Figure 5.17*a* would not be used where the vented gas was toxic, or valuable. In these circumstances the vent should be taken to a vent recovery system, such as a scrubber.

### 5.8.3. Flow control

Flow control is usually associated with inventory control in a storage tank or other equipment. There must be a reservoir to take up the changes in flow-rate.

To provide flow control on a compressor or pump running at a fixed speed and supplying a near constant volume output, a by-pass control would be used, as shown in Figures 5.18*a, b* (see p. 231).

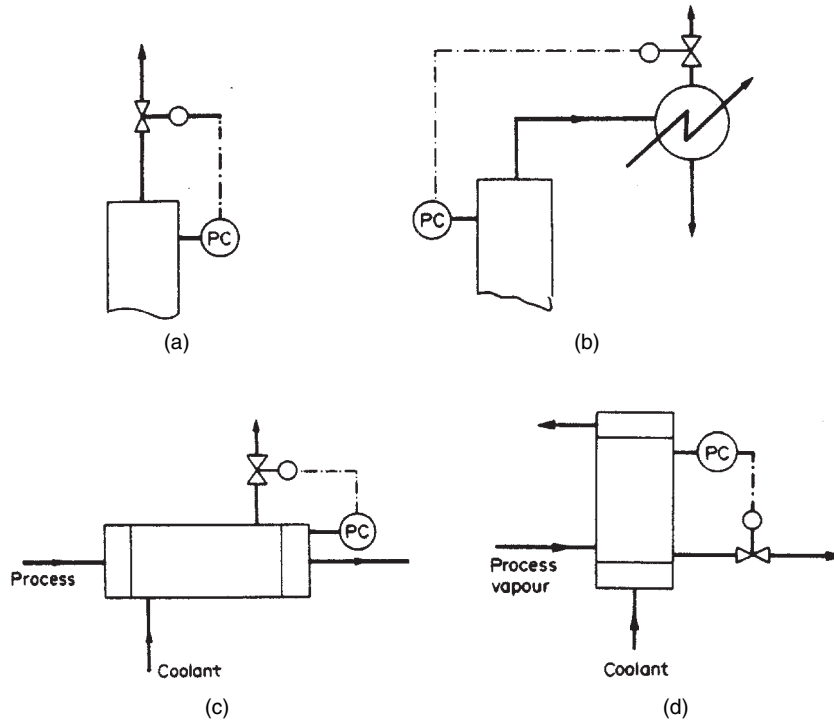


Figure 5.17. (a) Pressure control by direct venting (b) Venting of non-condensables after a condenser (c) Condenser pressure control by controlling coolant flow (d) Pressure control of a condenser by varying the heat-transfer area, area dependent on liquid level

#### 5.8.4. Heat exchangers

Figure 5.19a (see p. 232) shows the simplest arrangement, the temperature being controlled by varying the flow of the cooling or heating medium.

If the exchange is between two process streams whose flows are fixed, by-pass control will have to be used, as shown in Figure 5.19b (see p. 232).

##### **Condenser control**

Temperature control is unlikely to be effective for condensers, unless the liquid stream is sub-cooled. Pressure control is often used, as shown in Figure 5.17d, or control can be based on the outlet coolant temperature.

##### **Reboiler and vaporiser control**

As with condensers, temperature control is not effective, as the saturated vapour temperature is constant at constant pressure. Level control is often used for vaporisers; the controller controlling the steam supply to the heating surface, with the liquid feed to the vaporiser on flow control, as shown in Figure 5.20 (see p. 232). An increase in the feed results in an automatic increase in steam to the vaporiser to vaporise the increased flow and maintain the level constant.

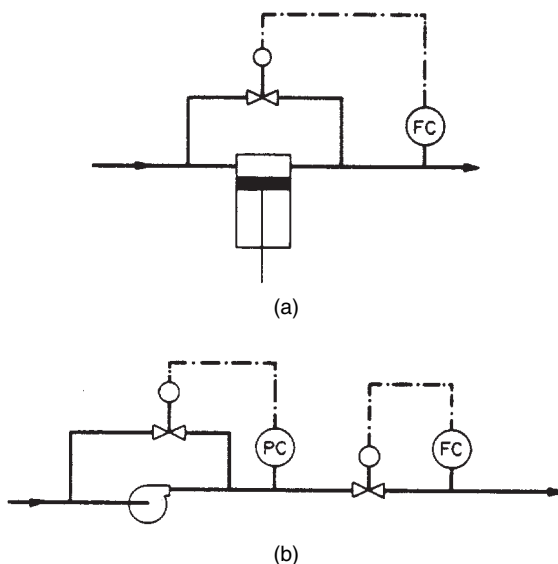


Figure 5.18. (a) Flow control for a reciprocating pump (b) Alternative scheme for a centrifugal compressor or pump

Reboiler control systems are selected as part of the general control system for the column and are discussed in Section 5.8.7.

### 5.8.5. Cascade control

With this arrangement, the output of one controller is used to adjust the set point of another. Cascade control can give smoother control in situations where direct control of the variable would lead to unstable operation. The “slave” controller can be used to compensate for any short-term variations in, say, a service stream flow, which would upset the controlled variable; the primary (master) controller controlling long-term variations. Typical examples are shown in Figure 5.22e (see p. 235) and 5.23 (see p. 235).

### 5.8.6. Ratio control

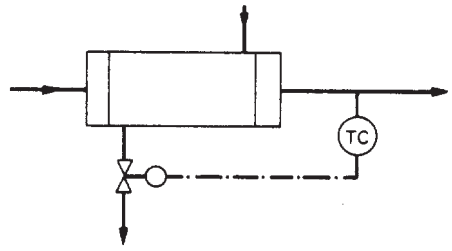
Ratio control can be used where it is desired to maintain two flows at a constant ratio; for example, reactor feeds and distillation column reflux. A typical scheme for ratio control is shown in Figure 5.21 (see p. 233).

### 5.8.7. Distillation column control

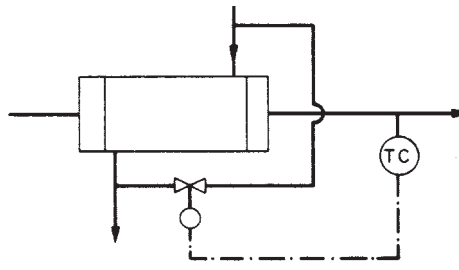
The primary objective of distillation column control is to maintain the specified composition of the top and bottom products, and any side streams; correcting for the effects of disturbances in:

1. Feed flow-rate, composition and temperature.
2. Steam supply pressure.





(a)



(b)

Figure 5.19. (a) Control of one fluid stream (b) By-pass control

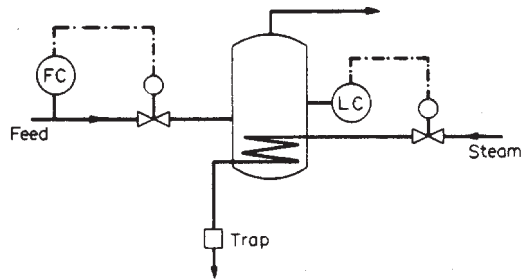


Figure 5.20. Vaporiser control

3. Cooling water pressure and header temperature.
4. Ambient conditions, which cause changes in internal reflux (see Chapter 11).

The compositions are controlled by regulating reflux flow and boil-up. The column overall material balance must also be controlled; distillation columns have little surge capacity (hold-up) and the flow of distillate and bottom product (and side-streams) must match the feed flows.

Shinsky (1984) has shown that there are 120 ways of connecting the five main parts of measured and controlled variables, in single loops. A variety of control schemes has been devised for distillation column control. Some typical schemes are shown in Figures 5.22a, b, c, d, e (see pp. 234, 235); ancillary control loops and instruments are not shown.

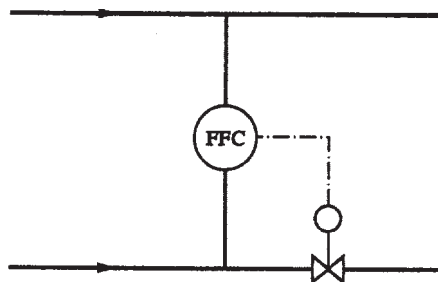


Figure 5.21. Ratio control

Distillation column control is discussed in detail by Parkins (1959), Bertrand and Jones (1961) and Shinskey (1984) Buckley *et al.* (1985).

Column pressure is normally controlled at a constant value. The use of variable pressure control to conserve energy has been discussed by Shinskey (1976).

The feed flow-rate is often set by the level controller on a preceding column. It can be independently controlled if the column is fed from a storage or surge tank.

Feed temperature is not normally controlled, unless a feed preheater is used.

Temperature is often used as an indication of composition. The temperature sensor should be located at the position in the column where the rate of change of temperature with change in composition of the key component is a maximum; see Parkins (1959). Near the top and bottom of the column the change is usually small. With multicomponent systems, temperature is not a unique function of composition.

Top temperatures are usually controlled by varying the reflux ratio, and bottom temperatures by varying the boil-up rate. If reliable on-line analysers are available they can be incorporated in the control loop, but more complex control equipment will be needed.

Differential pressure control is often used on packed columns to ensure that the packing operates at the correct loading; see Figure 5.22*d* (see p. 234).

Additional temperature indicating or recording points should be included up the column for monitoring column performance and for trouble shooting.

### 5.8.8. Reactor control

The schemes used for reactor control depend on the process and the type of reactor. If a reliable on-line analyser is available, and the reactor dynamics are suitable, the product composition can be monitored continuously and the reactor conditions and feed flows controlled automatically to maintain the desired product composition and yield. More often, the operator is the final link in the control loop, adjusting the controller set points to maintain the product within specification, based on periodic laboratory analyses.

Reactor temperature will normally be controlled by regulating the flow of the heating or cooling medium. Pressure is usually held constant. Material balance control will be necessary to maintain the correct flow of reactants to the reactor and the flow of products and unreacted materials from the reactor. A typical reactor control scheme is shown in Figure 5.23 (see p. 235).

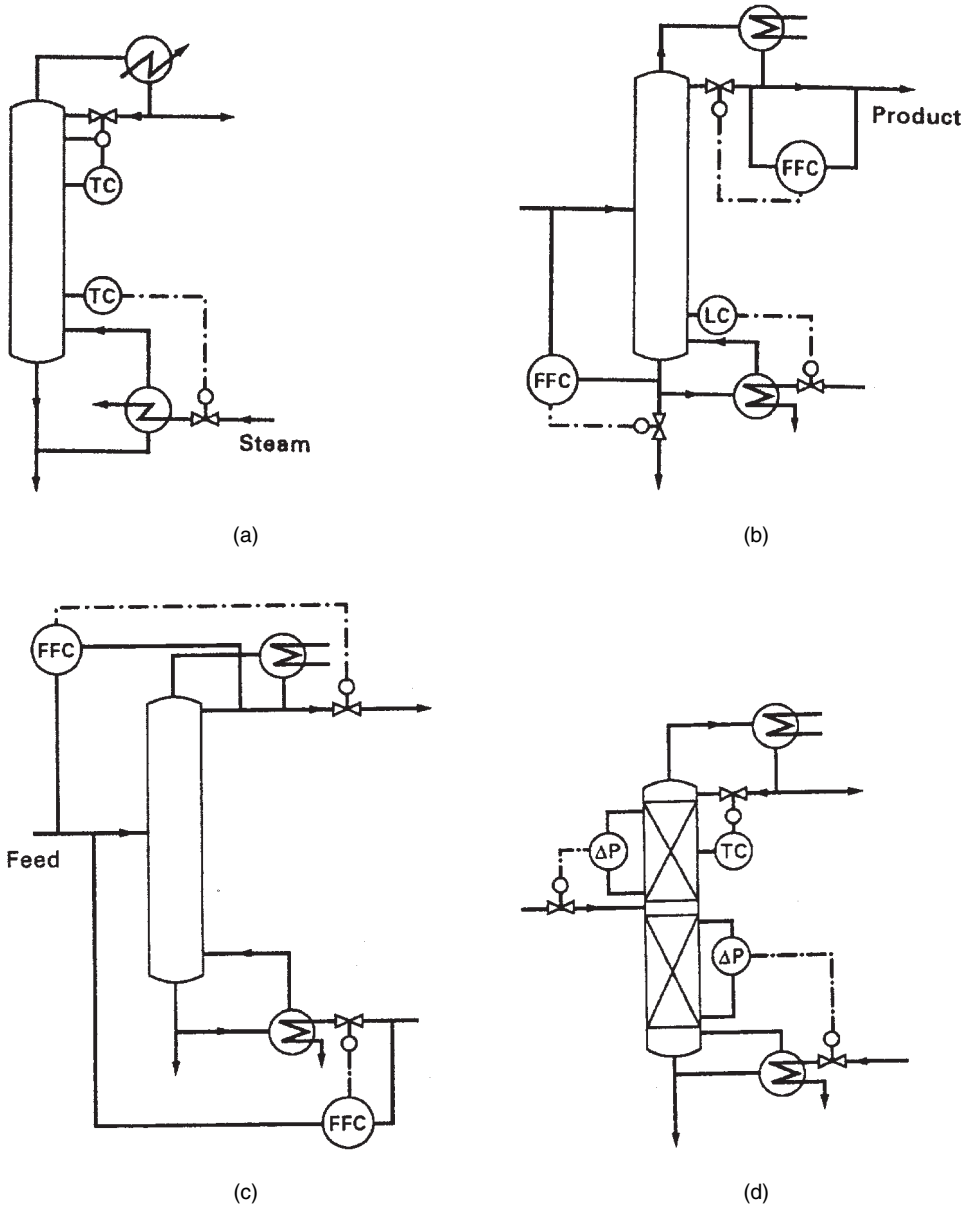


Figure 5.22. (a) Temperature pattern control. With this arrangement interaction can occur between the top and bottom temperature controllers (b) Composition control. Reflux ratio controlled by a ratio controller, or splitter box, and the bottom product as a fixed ratio of the feed flow (c) Composition control. Top product take-off and boil-up controlled by feed (d) Packed column, differential pressure control. Eckert (1964) discusses the control of packed columns

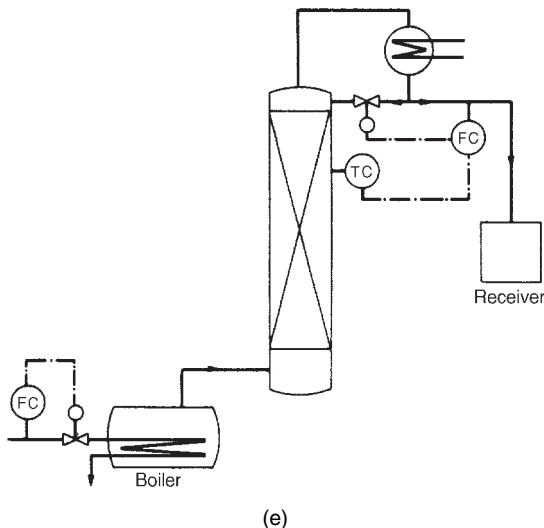


Figure 5.22. (e) Batch distillation, reflux flow cascaded with temperature to maintain constant top composition

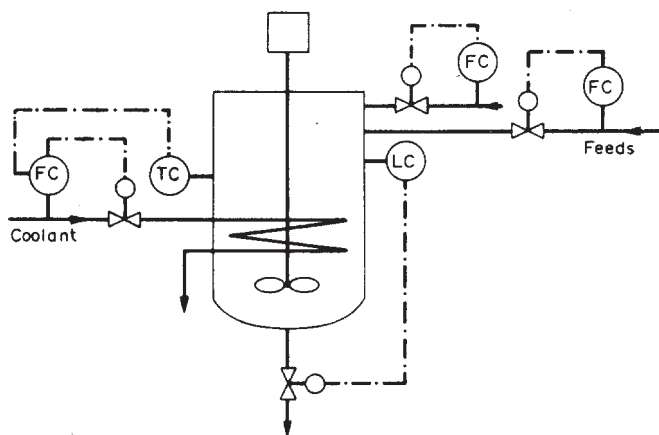


Figure 5.23. A typical stirred tank reactor control scheme, temperature: cascade control, and reagent: flow control

### 5.9. ALARMS AND SAFETY TRIPS, AND INTERLOCKS

Alarms are used to alert operators of serious, and potentially hazardous, deviations in process conditions. Key instruments are fitted with switches and relays to operate audible and visual alarms on the control panels and annunciator panels. Where delay, or lack of response, by the operator is likely to lead to the rapid development of a hazardous situation, the instrument would be fitted with a trip system to take action automatically to avert the hazard; such as shutting down pumps, closing valves, operating emergency systems.

The basic components of an automatic trip system are:

1. A sensor to monitor the control variable and provide an output signal when a preset value is exceeded (the instrument).
2. A link to transfer the signal to the actuator, usually consisting of a system of pneumatic or electric relays.
3. An actuator to carry out the required action; close or open a valve, switch off a motor.

A description of some of the equipment (hardware) used is given by Rasmussen (1975).

A safety trip can be incorporated in a control loop; as shown in Figure 5.24*a*. In this system the high-temperature alarm operates a solenoid valve, releasing the air on the pneumatic activator, closing the valve on high temperature. However, the safe operation of such a system will be dependent on the reliability of the control equipment, and for potentially hazardous situations it is better practice to specify a separate trip system; such as that shown in Figure 5.24*b*. Provision must be made for the periodic checking of the trip system to ensure that the system operates when needed.

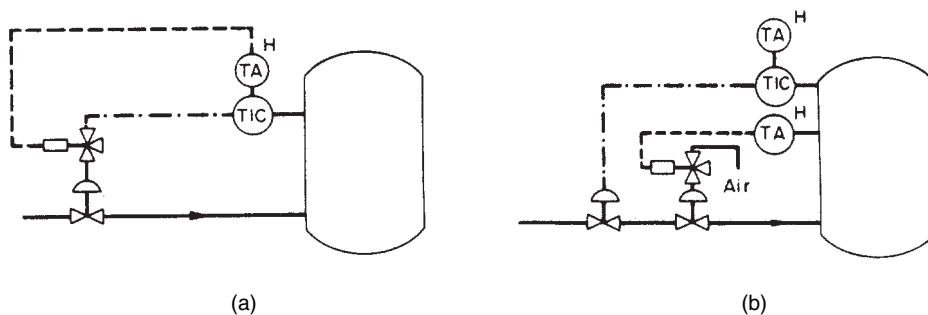


Figure 5.24. (a) Trip as part of control system (b) Separate shut-down trip

### Interlocks

Where it is necessary to follow a fixed sequence of operations—for example, during a plant start-up and shut-down, or in batch operations—interlocks are included to prevent operators departing from the required sequence. They may be incorporated in the control system design, as pneumatic or electric relays, or may be mechanical interlocks. Various proprietary special lock and key systems are available.

## 5.10. COMPUTERS AND MICROPROCESSORS IN PROCESS CONTROL

Computers are being increasingly used for data logging, process monitoring and control. They have largely superseded the strip charts and analogue controllers seen in older plant. The long instrument panels and “mimic” flow-chart displays have been replaced by intelligent video display units. These provide a window on the process. Operators

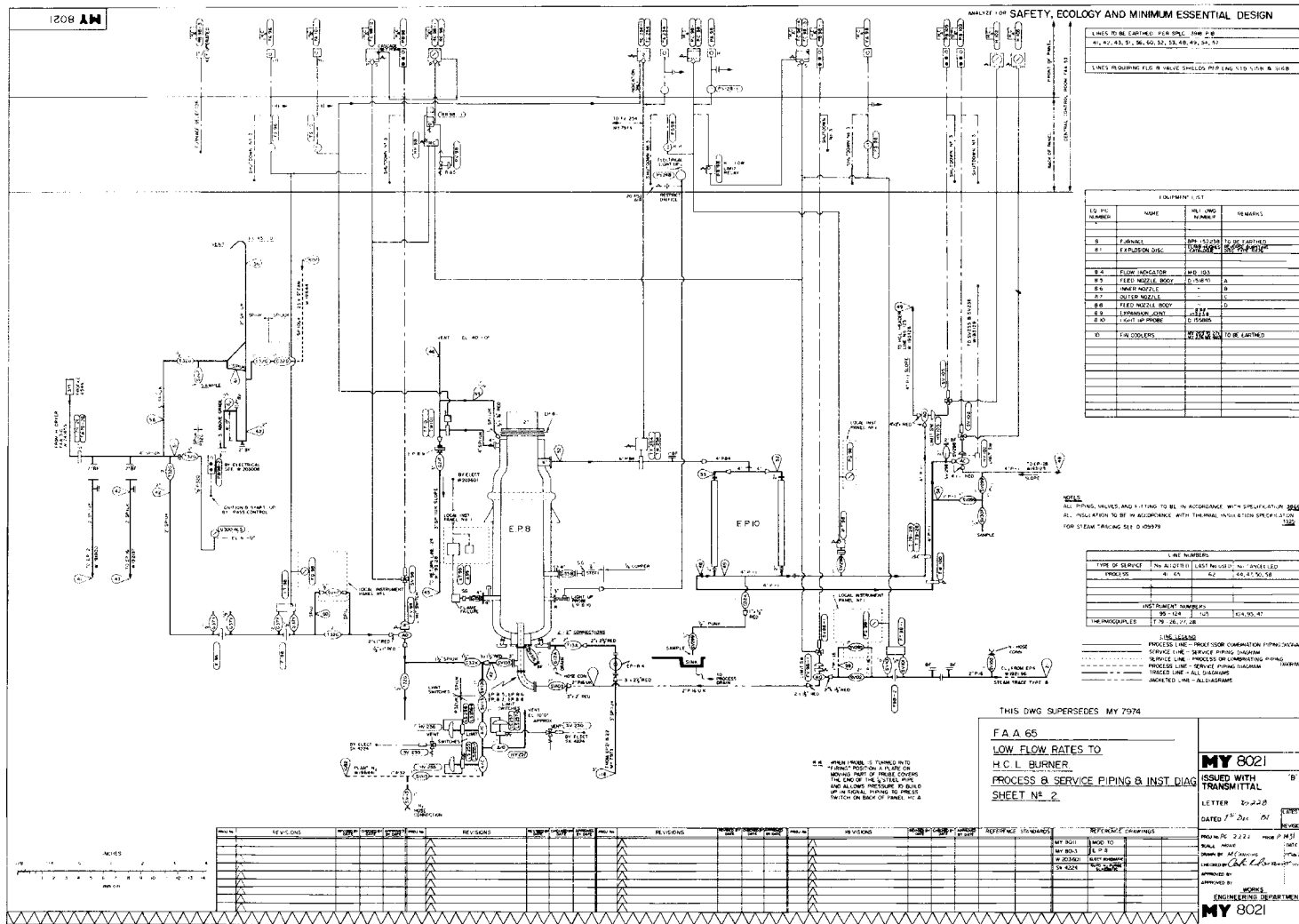


Figure 5.25. Piping and instrumentation diagram

and technical supervision can call up and display any section of the process to review the operating parameters and adjust control settings. Abnormal and alarm situations are highlighted and displayed.

Historical operating data is retained in the computer memory. Averages and trends can be displayed, for plant investigation and trouble shooting.

Software to continuously update and optimise plant performance can be incorporated in the computer control systems.

Programmable logic controllers are used for the control and interlocking of processes where a sequence of operating steps has to be carried out: such as, in batch processes, and in the start-up and shut down of continuous processes.

A detailed discussion of the application of digital computers and microprocessors in process control is beyond the scope of this volume. The use of computers and microprocessor based distributed control systems for the control of chemical process is covered by Kalani (1988).

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### British Standards

- BS 806: 1986 Ferrous pipes and piping for and in connection with land boilers.
- BS 1600: 1991 Dimension of steel pipes for the petroleum industry.
- BS 1646: 1984 Symbolic representation for process measurement control functions and instrumentation.  
 Part 1: 1977 Basic requirements.  
 Part 2: 1983 Specifications for additional requirements.  
 Part 3: 1984 Specification for detailed symbols for instrument interconnection diagrams.  
 Part 4: 1984 Specification for basic symbols for process computer, interface and shared display/control functions.

### American Standards

- USAS B31.1.0: The ASME standard code for pressure piping.
- ASA B31.3.0: The ASME code for petroleum refinery piping.

## 5.12. NOMENCLATURE

		Dimensions in MLT $\epsilon$
<i>A</i>	Plant attainment (hours operated per year)	—
<i>B</i>	Purchased cost factor, pipes	$\epsilon L^{-1}$
<i>a</i>	Capital charges factor, piping	—
<i>b</i>	Maintenance cost factor, piping	—
<i>Cf</i>	Annual pumping cost, piping	$\epsilon L^{-1} T^{-1}$
<i>Cp</i>	Capital cost, piping	$\epsilon L^{-1}$
<i>Ct</i>	Total annual cost, piping	$\epsilon L^{-1} T^{-1}$
<i>d</i>	Pipe diameter	<b>L</b>
<i>d<sub>i</sub></i>	Pipe inside diameter	<b>L</b>
<i>E</i>	Pump efficiency	—
<i>e</i>	Relative roughness	—



$F$	Installed cost factor, piping	—
$f$	Friction factor	—
$G$	Mass flow rate	$MT^{-1}$
$g$	Gravitational acceleration	$LT^{-2}$
$H$	Height of liquid above the pump suction	$L$
$h$	Pump head	$L$
$K$	Number of velocity heads	—
$L$	Pipe length	$L$
$m$	Mass flow-rate	$MT^{-1}$
$N$	Pump speed, revolutions per unit time	$T^{-1}$
$N_s$	Pump specific speed	—
$n$	Index relating pipe cost to diameter	—
$P$	Pressure	$ML^{-1}T^{-2}$
$P_f$	Pressure loss in suction piping	$ML^{-1}T^{-2}$
$P_s$	Safe working pressure	$ML^{-1}T^{-2}$
$P_v$	Vapour pressure of liquid	$ML^{-1}T^{-2}$
$\Delta P$	Difference in system pressures ( $P_1 - P_2$ )	$ML^{-1}T^{-2}$
$\Delta P_f$	Pressure drop <sup>†</sup>	$ML^{-1}T^{-2}$
$p$	Cost of power, pumping	—
$Q$	Volumetric flow rate	$L^3T^{-1}$
$R$	Shear stress on surface, pipes	$ML^{-1}T^{-2}$
$t$	Pipe wall thickness	$L$
$u$	Fluid velocity	$LT^{-1}$
$W$	Work done	$L^2T^{-2}$
$z$	Height above datum	$L$
$\Delta z$	Difference in elevation ( $z_1 - z_2$ )	$L$
$\eta$	Pump efficiency	—
$\rho$	Fluid density	$ML^{-3}$
$\mu$	Viscosity of fluid	$ML^{-1}T^{-1}$
$\sigma_d$	Design stress	$ML^{-1}T^{-2}$
$\sigma_s$	Safe working stress	$ML^{-1}T^{-2}$
Re	Reynolds number	—
$NPSH_{avail}$	Net positive suction head available at the pump suction	$L$
$NPSH_{reqd}$	Net positive suction head required at the pump suction	$L$

<sup>†</sup>Note: In Volumes 1 and 2 this symbol is used for pressure difference, and pressure drop (negative pressure gradient) indicated by a minus sign. In this chapter, as the symbol is only used for pressure drop, the minus sign is omitted for convenience.

## 5.13. PROBLEMS

5.1. Select suitable valve types for the following applications:

1. Isolating a heat exchanger.
2. Manual control of the water flow into a tank used for making up batches of sodium hydroxide solution.
3. The valves need to isolate a pump and provide emergency manual control on a by-pass loop.
4. Isolation valves in the line from a vacuum column to the steam ejectors producing the vacuum.
5. Valves in a line where cleanliness and hygiene are an essential requirement.

State the criterion used in the selection for each application.

**5.2.** Crude dichlorobenzene is pumped from a storage tank to a distillation column. The tank is blanketed with nitrogen and the pressure above the liquid surface is held constant at 0.1 bar gauge pressure. The minimum depth of liquid in the tank is 1 m.

The distillation column operates at a pressure of 500 mmHg (500 mm of mercury, absolute). The feed point to the column is 12 m above the base of the tank. The tank and column are connected by a 50 mm internal diameter commercial steel pipe, 200 m long. The pipe run from the tank to the column contains the following valves and fittings: 20 standard radius 90° elbows; two gate valves to isolate the pump (operated fully open); an orifice plate and a flow-control valve.

If the maximum flow-rate required is 20,000 kg/h, calculate the pump motor rating (power) needed. Take the pump efficiency as 70 per cent and allow for a pressure drop of 0.5 bar across the control valve and a loss of 10 velocity heads across the orifice.

Density of the dichlorobenzene 1300 kg/m<sup>3</sup>, viscosity 1.4 cp.

**5.3.** A liquid is contained in a reactor vessel at 115 bar absolute pressure. It is transferred to a storage vessel through a 50 mm internal diameter commercial steel pipe. The storage vessel is nitrogen blanketed and pressure above the liquid surface is kept constant at 1500 N/m<sup>2</sup> gauge. The total run of pipe between the two vessels is 200 m. The miscellaneous losses due to entry and exit losses, fittings, valves, etc., amount to 800 equivalent pipe diameters. The liquid level in the storage vessel is at an elevation 20 m *below* the level in the reactor.

A turbine is fitted in the pipeline to recover the excess energy that is available, over that required to transfer the liquid from one vessel to the other. Estimate the power that can be taken from the turbine, when the liquid transfer rate is 5000 kg/h. Take the efficiency of the turbine as 70%.

The properties of the fluid are: density 895 kg/m<sup>3</sup>, viscosity 0.76 mNm<sup>-2</sup>s.

**5.4.** A process fluid is pumped from the bottom of one distillation column to another, using a centrifugal pump. The line is standard commercial steel pipe 75 mm internal diameter. From the column to the pump inlet the line is 25 m long and contains six standard elbows and a fully open gate valve. From the pump outlet to the second column the line is 250 m long and contains ten standard elbows, four gate valves (operated fully open) and a flow-control valve. The fluid level in the first column is 4 m above the pump inlet. The feed point of the second column is 6 m above the pump inlet. The operating pressure in the first column is 1.05 bara and that of the second column 0.3 barg.

Determine the operating point on the pump characteristic curve when the flow is such that the pressure drop across the control valve is 35 kN/m<sup>2</sup>.

The physical properties of the fluid are: density 875 kg/m<sup>3</sup>, viscosity 1.46 mN m<sup>-2</sup>s.

Also, determine the NPSH, at this flow-rate, if the vapour pressure of the fluid at the pump suction is 25 kN/m<sup>2</sup>.

Pump characteristic

Flow-rate, m <sup>3</sup> /h	0.0	18.2	27.3	36.3	45.4	54.5	63.6
Head, m of liquid	32.0	31.4	30.8	29.0	26.5	23.2	18.3

**5.5.** A polymer is produced by the emulsion polymerisation of acrylonitrile and methyl methacrylate in a stirred vessel. The monomers and an aqueous solution of catalyst are fed to the polymerisation reactor continuously. The product is withdrawn from the base of the vessel as a slurry.

Devise a control system for this reactor, and draw up a preliminary piping and instrument diagram. The follow points need to be considered:

1. Close control of the reactor temperature is required.
  2. The reactor runs 90 per cent full.
  3. The water and monomers are fed to the reactor separately.
  4. The emulsion is a 30 per cent mixture of monomers in water.
  5. The flow of catalyst will be small compared with the water and monomer flows.
  6. Accurate control of the catalyst flow is essential.
- 5.6.** Devise a control system for the distillation column described in Chapter 11, Example 11.2. The flow to the column comes from a storage tank. The product, acetone, is sent to storage and the waste to an effluent pond. It is essential that the specifications on product and waste quality are met.

## CHAPTER 6

# *Costing and Project Evaluation*

### 6.1. INTRODUCTION

Cost estimation is a specialised subject and a profession in its own right. The design engineer, however, needs to be able to make quick, rough, cost estimates to decide between alternative designs and for project evaluation. Chemical plants are built to make a profit, and an estimate of the investment required and the cost of production are needed before the profitability of a project can be assessed.

In this chapter the various components that make up the capital cost of a plant and the components of the operating costs are discussed, and the techniques used for estimating reviewed briefly. Simple costing methods and some cost data are given, which can be used to make preliminary estimates of capital and operating costs at the flow-sheet stage. They can also be used to cost out alternative processing schemes and equipment.

For a more detailed treatment of the subject the reader should refer to the numerous specialised texts that have been published on cost estimation. The following books are particularly recommended: Happle and Jordan (1975) and Guthrie (1974), Page (1984), Garrett (1989).

### 6.2. ACCURACY AND PURPOSE OF CAPITAL COST ESTIMATES

The accuracy of an estimate depends on the amount of design detail available: the accuracy of the cost data available; and the time spent on preparing the estimate. In the early stages of a project only an approximate estimate will be required, and justified, by the amount of information by then developed.

Capital cost estimates can be broadly classified into three types according to their accuracy and purpose:

1. Preliminary (approximate) estimates, accuracy typically  $\pm 30$  per cent, which are used in initial feasibility studies and to make coarse choices between design alternatives. They are based on limited cost data and design detail.
2. Authorisation (Budgeting) estimates, accuracy typically  $\pm 10$ – $15$  per cent. These are used for the authorisation of funds to proceed with the design to the point where an accurate and more detailed estimate can be made. Authorisation may also include funds to cover cancellation charges on any long delivery equipment ordered at this stage of the design to avoid delay in the project. In a contracting organisation this type of estimate could be used with a large contingency factor to obtain a price for tendering. Normally, however, an accuracy of about  $\pm 5$  per cent would be needed

and a more detailed estimate would be made, if time permitted. With experience, and where a company has cost data available from similar projects, estimates of acceptable accuracy can be made at the flow-sheet stage of the project. A rough P and I diagram and the approximate sizes of the major items of equipment would also be needed.

3. Detailed (Quotation) estimates, accuracy  $\pm 5$ –10 per cent, which are used for project cost control and estimates for fixed price contracts. These are based on the completed (or near complete) process design, firm quotations for equipment, and a detailed breakdown and estimation of the construction cost.

The cost of preparing an estimate increases from about 0.1 per cent of the total project cost for  $\pm 30$  per cent accuracy, to about 2 per cent for a detailed estimate with an accuracy of  $\pm 5$  per cent.

### 6.3. FIXED AND WORKING CAPITAL

Fixed capital is the total cost of the plant ready for start-up. It is the cost paid to the contractors.

It includes the cost of:

1. Design, and other engineering and construction supervision.
2. All items of equipment and their installation.
3. All piping, instrumentation and control systems.
4. Buildings and structures.
5. Auxiliary facilities, such as utilities, land and civil engineering work.

It is a once-only cost that is not recovered at the end of the project life, other than the scrap value.

Working capital is the additional investment needed, over and above the fixed capital, to start the plant up and operate it to the point when income is earned.

It includes the cost of:

1. Start-up.
2. Initial catalyst charges.
3. Raw materials and intermediates in the process.
4. Finished product inventories.
5. Funds to cover outstanding accounts from customers.

Most of the working capital is recovered at the end of the project. The total investment needed for a project is the sum of the fixed and working capital.

Working capital can vary from as low as 5 per cent of the fixed capital for a simple, single-product, process, with little or no finished product storage; to as high as 30 per cent for a process producing a diverse range of product grades for a sophisticated market, such as synthetic fibres. A typical figure for petrochemical plants is 15 per cent of the fixed capital.

Methods for estimating the working capital requirement are given by Bechtel (1960), Lyda (1972) and Scott (1978).

## 6.4. COST ESCALATION (INFLATION)

The cost of materials and labour has been subject to inflation since Elizabethan times. All cost-estimating methods use historical data, and are themselves forecasts of future costs. Some method has to be used to update old cost data for use in estimating at the design stage, and to forecast the future construction cost of the plant.

The method usually used to update historical cost data makes use of published cost indices. These relate present costs to past costs, and are based on data for labour, material and energy costs published in government statistical digests.

$$\text{Cost in year A} = \text{Cost in year B} \times \frac{\text{Cost index in year A}}{\text{Cost index in year B}} \quad (6.1)$$

To get the best estimate, each job should be broken down into its components and separate indices used for labour and materials. It is often more convenient to use the composite indices published for various industries in the trade journals. These produce a weighted average index combining the various components in proportions considered typical for the particular industry. Such an index for the chemical industry in the United Kingdom is published in the journal *Process Engineering*, Anon. (2004). The composition of this index is:

$$C = 0.45E_q + 0.1C_i + 0.19C_n + 0.26D_i$$

where C = the composite index  
 C<sub>i</sub> = civil engineering index  
 C<sub>n</sub> = site engineering index  
 D<sub>i</sub> = design index

The base year used for the index is revised about every 5 years. The base for the current index is January 2000 = 100; see Anon. (2002). Care must be taken when updating costs over a period that includes a change in the index base; see Example 6.1.

*The Process Engineering index*, over a ten-year period (January to January), is shown in Figure 6.1a.

*Process Engineering* also publishes monthly cost indices for several other countries, including the United States, Japan, Australia and many of the EU countries.

A composite index for the United States process plant industry is published monthly in the journal *Chemical Engineering*, the CPE plant cost index. This journal also publishes the Marshall and Swift index (M and S equipment cost index), base year 1926. The CPE index over a ten-year period is shown in Figure 6.1b.

All cost indices should be used with caution and judgement. They do not necessarily relate the true make-up of costs for any particular piece of equipment or plant; nor the effect of supply and demand on prices. The longer the period over which the correlation is made the more unreliable the estimate. Between 1970 and 1990 prices rose dramatically. Since then the annual rise has slowed down and is now averaging around 2 to 3 per cent per year.

To estimate the future cost of a plant some prediction has to be made of the future annual rate of inflation. This can be based on the extrapolation of one of the published indices, tempered by the engineer's own assessment of what the future may hold.

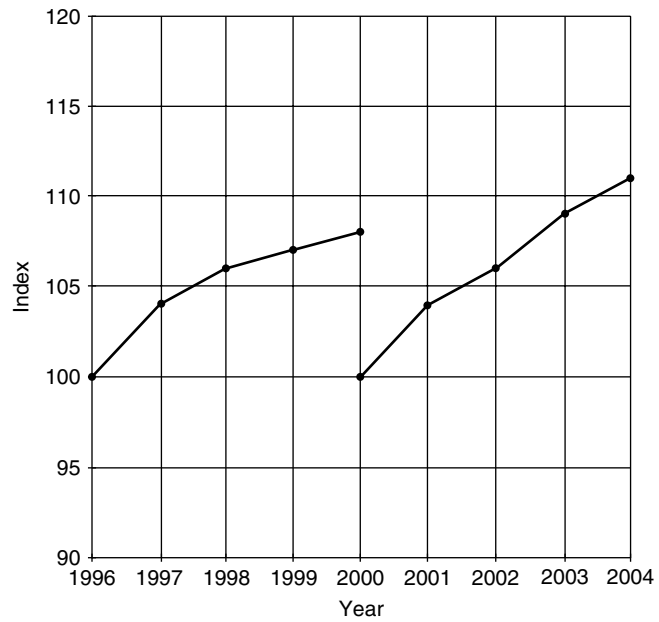


Figure 6.1a. Process Engineering index

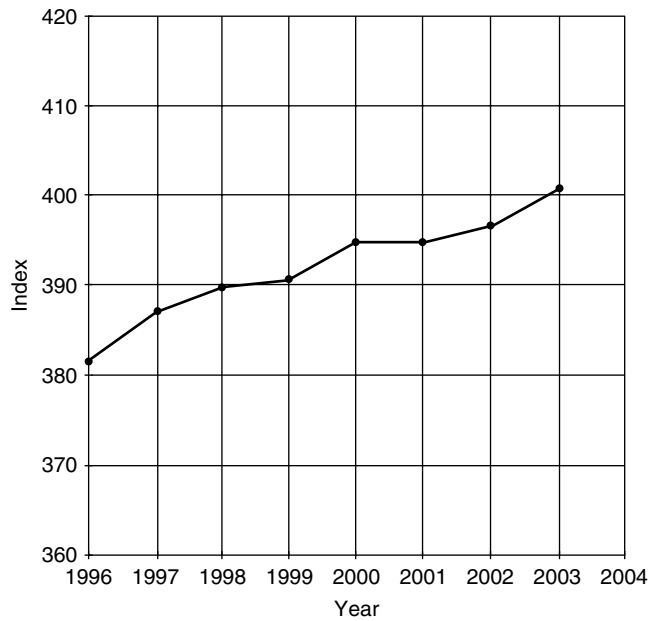


Figure 6.1b. CPE index

**Example 6.1**

The purchased cost of a shell and tube heat exchanger, carbon shell, stainless steel tubes, heat transfer area 500 m<sup>2</sup>, was £7600 in January 1998; estimate the cost in January 2006. Use the *Process Engineering* plant index.

**Solution**

From Figure 6.1:

$$\begin{aligned} \text{Index in 1998} &= 106 \\ 2000 &= 108, 100 \text{ (change of base)} \\ 2004 &= 111 \end{aligned}$$

So, estimated cost in January 2000 =  $7600 \times 108/106 = \text{£}7743$ ,

and in 2004 =  $7743 \times 111/100 = \text{£}8595$

From Figure 6.1, the average increase in costs is about 2.5 per cent per year. Use this value to predict the exchanger cost in 2006.

Cost in 2006 =  $8595 \times (1.025)^2 = \text{£}9030$

Say £9000.

**6.5. RAPID CAPITAL COST ESTIMATING METHODS****6.5.1. Historical costs**

An approximate estimate of the capital cost of a project can be obtained from a knowledge of the cost of earlier projects using the same manufacturing process. This method can be used prior to the preparation of the flow-sheets to get a quick estimate of the investment likely to be required.

The capital cost of a project is related to capacity by the equation

$$C_2 = C_1 \left( \frac{S_2}{S_1} \right)^n \quad (6.2)$$

where  $C_2$  = capital cost of the project with capacity  $S_2$ ,

$C_1$  = capital cost of the project with capacity  $S_1$ .

The value of the index  $n$  is traditionally taken as 0.6; the well-known six-tenths rule. This value can be used to get a rough estimate of the capital cost if there are not sufficient data available to calculate the index for the particular process. Estrup (1972) gives a critical review of the six-tenths rule. Equation 6.2 is only an approximation, and if sufficient data are available the relationship is best represented on a log-log plot. Garrett (1989) has published capital cost-plant capacity curves for over 250 processes.

**Example 6.2**

Obtain a rough estimate of the cost of a plant to produce 750 tonnes per day of sulphuric acid, from sulphur. Use the costs given by Garrett (1989) reproduced in Figure 6.2.



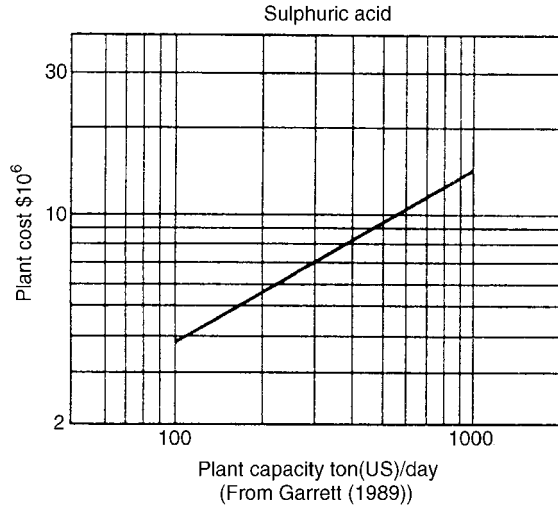


Figure 6.2. Capital Cost v. Capacity

### Solution

Garret's units are US dollars and US tons, and refer to 1987 (*Chemical Engineering Index* quoted as 320).

$$1 \text{ US ton} = 2000 \text{ lb} = 0.91 \text{ tonne (1000 kg)}$$

$$\text{So, } 750 \text{ tonne per day} = 750/0.91 = 824 \text{ US t/d}$$

From Figure 6.2 the fixed capital cost for this capacity, for production from sulphur, is  $13 \times 10^6$  US dollars.

There are two possible ways to convert to UK costs:

1. Convert at the 1987 exchange rate and update using a UK index.
2. Update using a US index and convert using the current exchange rate.

1. In 1987 (January) the rate of exchange was  $\$1.64 = \text{£}1$ , and UK and US cost can be taken as roughly equivalent.

$$1987 \text{ cost} = \frac{13 \times 10^6}{1.64} = \text{£}7.93 \times 10^6$$

Updating this cost using the index published in *Process Engineering* (basis 100 at end 1990)

$$\text{Index } 1987 \text{ (January)} = 78$$

$$2004 \text{ (January)} = 154 \text{ (basis adjusted to 1990)}$$

$$\text{So, capital cost of plant early 2004} = 7.93 \times 10^6 \times \frac{154}{78} = \text{£}15.67 \times 10^6$$

$$\text{say, } \underline{\underline{\text{£}16,000,000}}$$

2. Garrett quotes the *Chemical Engineering Index* for his costs as 320 (January 1987).

The value in January 2004 was, approximately, 405, so the dollar cost of the plant in early 2004 will be:

$$13 \times 10^6 \times \frac{405}{320} = \$16.45 \times 10^6$$

The rate of exchange in January 2004 was \$1.82, so the cost in pounds sterling will be

$$\frac{16.45 \times 10^6}{1.82} = \text{£}9.04 \times 10^6$$

say, \$9,000,000

Widely different from that estimated by method 1. This is not surprising as inflation in the UK has been very much greater than that in the US over this period.

Where UK, or other local, indexes and historical exchange rates are available, it is probably better to convert costs to the local currency using the rate of exchange ruling at the date of the costs and update using the local index: method 1 in the Example 6.2. In the United Kingdom historical values for exchange rates can be found in the government publication *Economic Trends* (Central Statistical Office, HMSO). Current and historical values for most currencies can be found on the Internet/World Wide Web.

As a rough guide US costs can be taken as equivalent to local prices, converted to local currency, for Western European countries, but construction costs may be significantly greater in less developed parts of the world.

Location factors can be used to make allowance for the variation in costs in different countries; see IChemE (1987).

### 6.5.2. Step counting methods

Step counting estimating methods provide a way of making a quick, *order of magnitude*, estimate of the capital cost of a proposed project.

The technique is based on the premise that the capital cost is determined by a number of significant processing steps in the overall process. Factors are usually included to allow for the capacity, and complexity of the process: material of construction, yield, operating pressure and temperature.

A number of workers have published correlations based on a step counting approach: Taylor (1977), Wilson (1971). These and other correlations are reviewed and compared in the Institution of Chemical Engineers booklet, IChemE (1988).

Bridgwater, IChemE (1988), gives a developed relatively simple correlation for plants that are predominantly liquid and/or solid phase handling processes.

His equation, adjusted to 2004 prices is:

for plant capacities under 60,000 tonne per year:

$$C = 150,000 N (Q/s)^{0.30} \quad (6.3)$$

and above 60,000 t/y:

$$C = 170 N (Q/s)^{0.675} \quad (6.4)$$

where C = capital cost in pounds sterling

N = Number of functional units

$Q$  = plant capacity, tonne per year

$s$  = reactor conversion

Reactor conversion is defined as:

$$s = \frac{\text{mass of desired product}}{\text{mass reactor input}}$$

Timms, IChemE (1988) gives a simple equation for gas phase processes; updated to 1998:

$$C = 9000 N Q^{0.615} \quad (6.5)$$

where the symbols are the same as for equations 6.3 and 6.4.

In US dollars

$$C' = 14,000 N Q^{0.615} \quad (6.5a)$$

Where  $C'$  = capital cost in US dollars

### Example 6.3

Estimate the capital cost for the nitric acid plant shown in Figure 4.2, Chapter 4.

### Solution

Number of significant processing steps 6.

Capacity 100,000 tonne per year

$$C = 9000 \times 6 \times 100,000^{0.615} = 64.2 \times 10^6 \quad (6.5)$$

say, £65 million.

$$C' = 14,000 \times 6 \times 100,000^{0.615} = 99.8 \times 10^6$$

say, \$100 million.

Clearly, step counting methods can only, at best, give a very approximate idea of the probable cost of a plant. They are useful in the conceptual stage of process design, when comparisons between alternative process routes are being made.

## 6.6. THE FACTORIAL METHOD OF COST ESTIMATION

Capital cost estimates for chemical process plants are often based on an estimate of the purchase cost of the major equipment items required for the process, the other costs being estimated as factors of the equipment cost. The accuracy of this type of estimate will depend on what stage the design has reached at the time the estimate is made, and on the reliability of the data available on equipment costs. In the later stages of the project design, when detailed equipment specifications are available and firm quotations have been obtained, an accurate estimation of the capital cost of the project can be made.

### 6.6.1. Lang factors

The factorial method of cost estimation is often attributed to Lang (1948). The fixed capital cost of the project is given as a function of the total purchase equipment cost by the equation:

$$Cf = f_L Ce \quad (6.6)$$

where  $Cf$  = fixed capital cost,

$Ce$  = the total delivered cost of all the major equipment items: storage tanks, reaction vessels, columns, heat exchangers, etc.,

$f_L$  = the “Lang factor”, which depends on the type of process.

$f_L = 3.1$  for predominantly solids processing plant

$f_L = 4.7$  for predominantly fluids processing plant

$f_L = 3.6$  for a mixed fluids-solids processing plant

The values given above should be used as a guide; the factor is best derived from an organisation’s own cost files.

Equation 6.6 can be used to make a quick estimate of capital cost in the early stages of project design, when the preliminary flow-sheets have been drawn up and the main items of equipment roughly sized.

### 6.6.2. Detailed factorial estimates

To make a more accurate estimate, the cost factors that are compounded into the “Lang factor” are considered individually. The direct-cost items that are incurred in the construction of a plant, in addition to the cost of equipment are:

1. Equipment erection, including foundations and minor structural work.
2. Piping, including insulation and painting.
3. Electrical, power and lighting.
4. Instruments, local and control room.
5. Process buildings and structures.
6. Ancillary buildings, offices, laboratory buildings, workshops.
7. Storages, raw materials and finished product.
8. Utilities (Services), provision of plant for steam, water, air, firefighting services (if not costed separately).
9. Site, and site preparation.

The contribution of each of these items to the total capital cost is calculated by multiplying the total purchased equipment by an appropriate factor. As with the basic “Lang factor”, these factors are best derived from historical cost data for similar processes. Typical values for the factors are given in several references, Happle and Jordan (1975) and Garrett (1989). Guthrie (1974), splits the costs into the material and labour portions and gives separate factors for each. In a booklet published by the Institution of Chemical Engineers, IChemE (1988), the factors are shown as a function of plant size and complexity.

The accuracy and reliability of an estimate can be improved by dividing the process into sub-units and using factors that depend on the function of the sub-units; see Guthrie (1969). In Guthrie’s detailed method of cost estimation the installation, piping and

instrumentation costs for each piece of equipment are costed separately. Detailed costing is only justified if the cost data available are reliable and the design has been taken to the point where all the cost items can be identified and included.

Typical factors for the components of the capital cost are given in Table 6.1. These can be used to make an approximate estimate of capital cost using equipment cost data published in the literature.

In addition to the direct cost of the purchase and installation of equipment, the capital cost of a project will include the indirect costs listed below. These can be estimated as a function of the direct costs.

### **Indirect costs**

1. Design and engineering costs, which cover the cost of design and the cost of “engineering” the plant: purchasing, procurement and construction supervision. Typically 20 per cent to 30 per cent of the direct capital costs.
2. Contractor’s fees, if a contractor is employed his fees (profit) would be added to the total capital cost and would range from 5 per cent to 10 per cent of the direct costs.
3. Contingency allowance, this is an allowance built into the capital cost estimate to cover for *unforeseen* circumstances (labour disputes, design errors, adverse weather). Typically 5 per cent to 10 per cent of the direct costs.

The indirect cost factors are included in Table 6.1.

The capital cost required for the provision of utilities and other plant services will depend on whether a new (green field) site is being developed, or if the plant is to be built on an existing site and will make use of some of the existing facilities. The term

Table 6.1. Typical factors for estimation of project fixed capital cost

Item	Process type		
	Fluids	Fluids– solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
$f_1$ Equipment erection	0.4	0.45	0.50
$f_2$ Piping	0.70	0.45	0.20
$f_3$ Instrumentation	0.20	0.15	0.10
$f_4$ Electrical	0.10	0.10	0.10
$f_5$ Buildings, process	0.15	0.10	0.05
* $f_6$ Utilities	0.50	0.45	0.25
* $f_7$ Storages	0.15	0.20	0.25
* $f_8$ Site development	0.05	0.05	0.05
* $f_9$ Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC)			
PPC = PCE (1 + $f_1$ + ... + $f_9$ )			
= PCE ×	3.40	3.15	2.80
$f_{10}$ Design and Engineering	0.30	0.25	0.20
$f_{11}$ Contractor’s fee	0.05	0.05	0.05
$f_{12}$ Contingency	0.10	0.10	0.10
Fixed capital = PPC (1 + $f_{10}$ + $f_{11}$ + $f_{12}$ )			
= PPC ×	1.45	1.40	1.35

\*Omitted for minor extensions or additions to existing sites.

“battery limits” is used to define a contractor’s responsibility. The main processing plant, within the battery limits, would normally be built by one contractor. The utilities and other ancillary equipment would often be the responsibility of other contractors and would be said to be outside the battery limits. They are often also referred to as “off-sites”.

## 6.7. ESTIMATION OF PURCHASED EQUIPMENT COSTS

The cost of the purchased equipment is used as the basis of the factorial method of cost estimation and must be determined as accurately as possible. It should preferably be based on recent prices paid for similar equipment.

The relationship between size and cost given in equation 6.2 can also be used for equipment, but the relationship is best represented by a log-log plot if the size range is wide. A wealth of data has been published on equipment costs; see Guthrie (1969, 1974), Hall *et al.* (1982), Page (1984), Ulrich (1984), Garrett (1989) and Peters *et al.* (2003). Articles giving the cost of process equipment are frequently published in the journals *Chemical Engineering* and *Hydrocarbon Processing*. Equipment prices can also be found on various web sites, such as: MatchesMSN@msn.com.

The cost of specialised equipment, which cannot be found in the literature, can usually be estimated from the cost of the components that make up the equipment. For example, a reactor design is usually unique for a particular process but the design can be broken down into standard components (vessels, heat-exchange surfaces, spargers, agitators) the cost of which can be found in the literature and used to build up an estimate of the reactor cost.

Pikulik and Diaz (1977) give a method of costing major equipment items from cost data on the basic components: shells, heads, nozzles, and internal fittings. Purohit (1983) gives a detailed procedure for estimating the cost of heat exchangers.

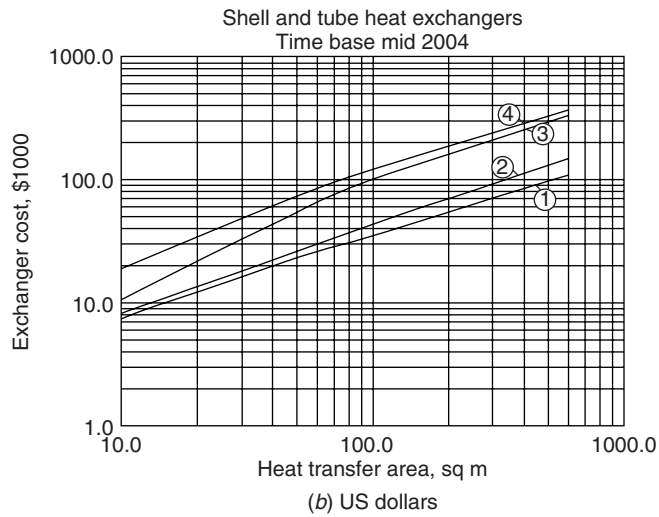
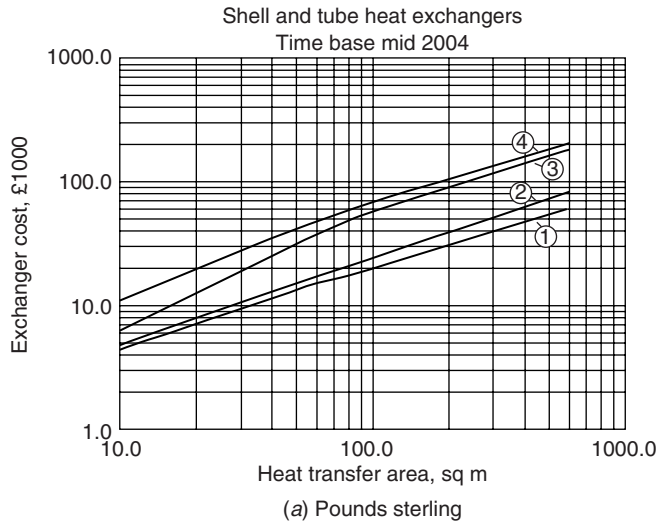
Almost all the information on costs available in the open literature is in American journals and refers to dollar prices in the US. Some UK equipment prices were published in the journals *British Chemical Engineering* and *Chemical and Process Engineering* before they ceased publication. The only comprehensive collection of UK prices available is given in the Institution of Chemical Engineers booklet, IChemE (2000).

Up to 1970 US and UK prices for equipment could be taken as roughly equivalent, converting from dollars to pounds using the rate of exchange ruling on the date the prices were quoted. Since 1970 the rate of inflation in the US has been significantly lower than in the UK, and rates of exchange have fluctuated since the pound was floated in 1972.

If it can be assumed that world market forces will level out the prices of equipment, the UK price can be estimated from the US price by bringing the cost up to date using a suitable US price index, converting to pounds sterling at the current rate of exchange, and adding an allowance for freight and duty.

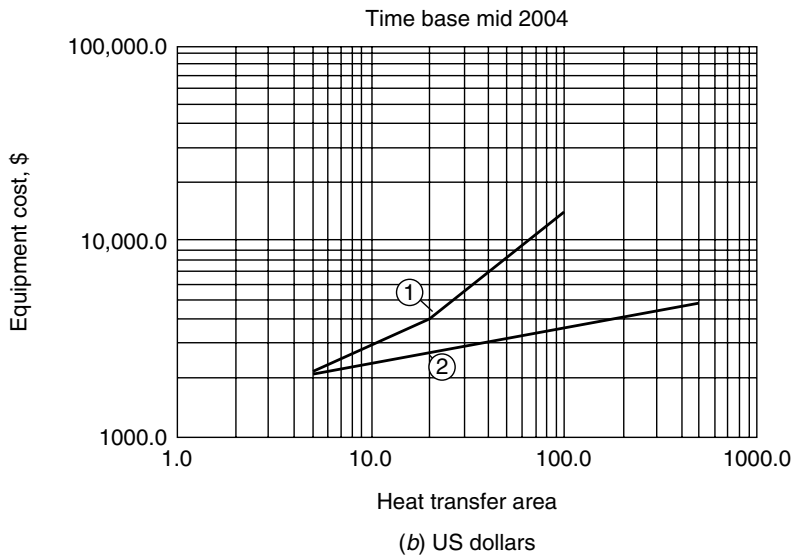
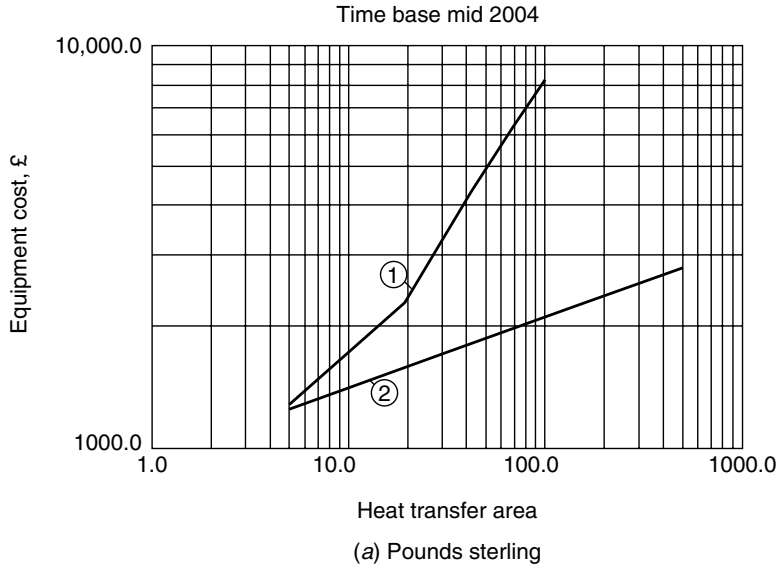
If an estimate is being made to compare two processes, the costing can be done in dollars and any conclusion drawn from the comparison should still be valid for the United Kingdom and other countries.

The cost data given in Figures 6.3 to 6.7, and Table 6.2 have been compiled from various sources. They can be used to make preliminary estimates. The base date is mid-2004, and the prices are thought to be accurate to within  $\pm 25$  per cent.



Materials		Pressure factors	Type factors	
Shell	Tubes			
① Carbon steel	Carbon steel	1–10 bar × 1.0	Floating head	× 1.0
② C.S.	Brass	10–20 × 1.1	Fixed tube sheet	× 0.8
③ C.S.	Stainless steel	20–30 × 1.25	U tube	× 0.85
④ S.S.	S.S.	30–50 × 1.3	Kettle	× 1.3
		50–70 × 1.5		

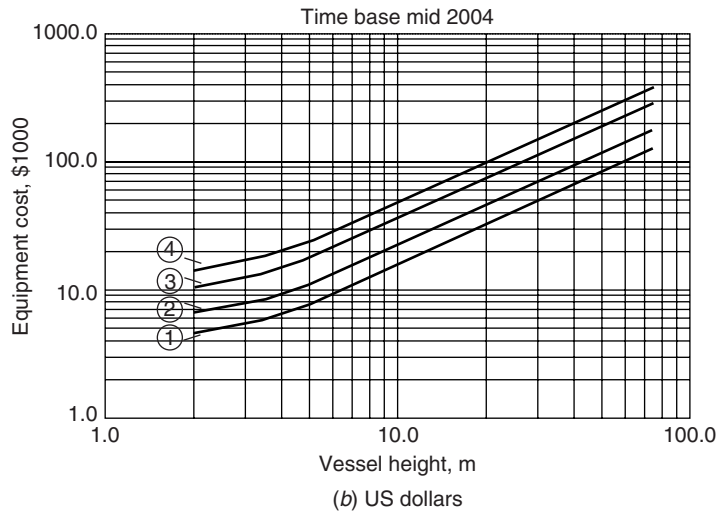
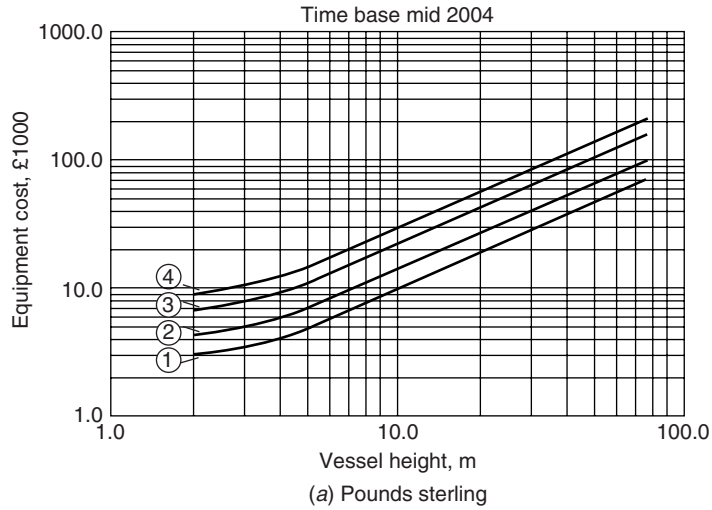
Figure 6.3a, b. Shell and tube heat exchangers. Time base mid-2004  
Purchased cost = (bare cost from figure) × Type factor × Pressure factor



Type	Area scale	Material
(1) Gasketed plate	m <sup>2</sup>	Stainless steel
(2) Double pipe	m <sup>2</sup> × 10	Carbon steel

Figure 6.4a, b. Gasketed plate and frame and double pipe heat exchangers, Time base mid-2004

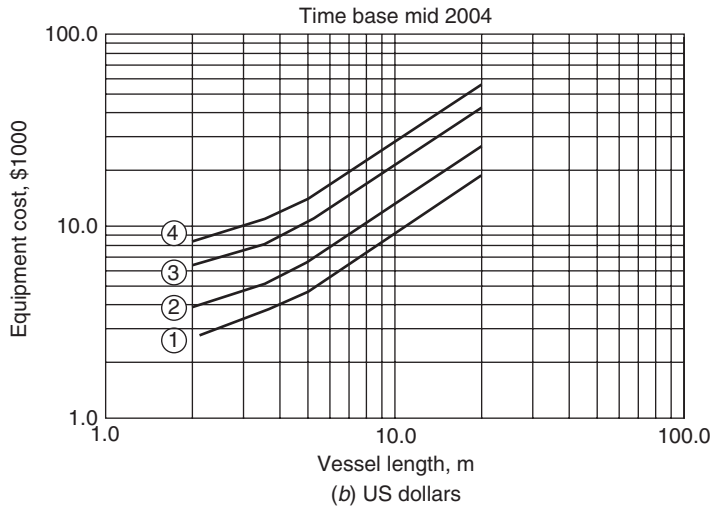
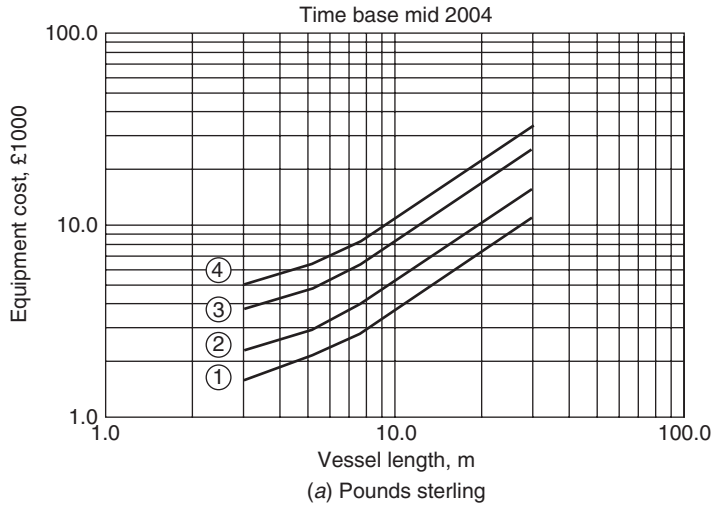




Diameter, m		Material factors	Pressure factors
①—0.5	③—2.0	C.S. × 1.0	1–5 bar × 1.0
		S.S. × 2.0	5–10 × 1.1
②—1.0	④—3.0	Monel × 3.4	10–20 × 1.2
		S.S. clad × 1.5	20–30 × 1.4
		Monel clad × 2.1	30–40 × 1.6
			40–50 × 1.8
			50–60 × 2.2

Temperature up to 300°C

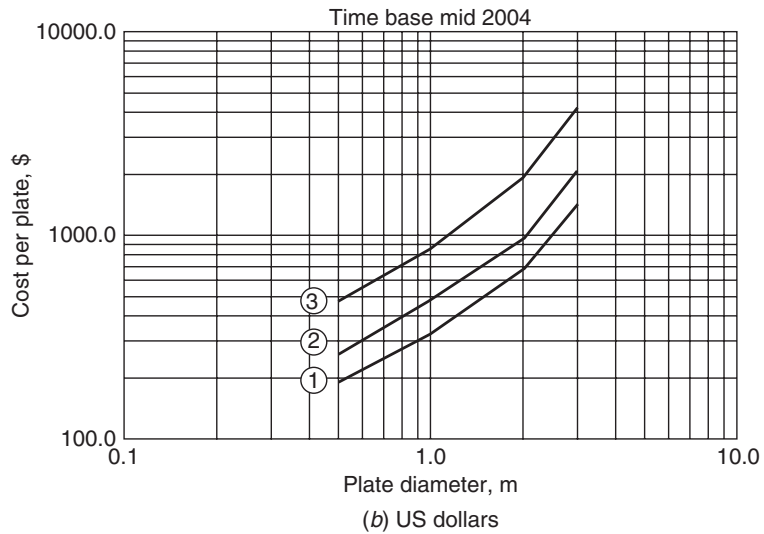
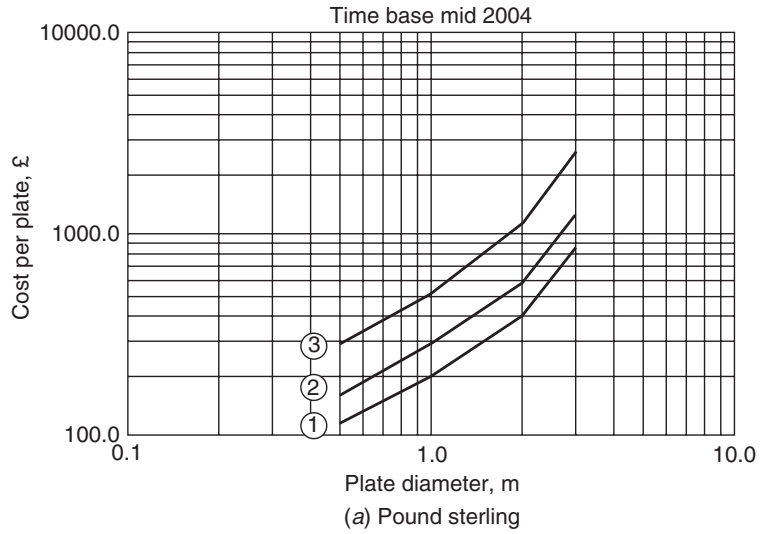
Figure 6.5a, b. Vertical pressure vessels. Time base mid-2004.  
 Purchased cost = (bare cost from figure) × Material factor × Pressure factor



Diameter, m		Material factors	Pressure factors
① — 0.5	③ — 2.0	C.S. × 1.0	1–5 bar × 1.0
② — 1.0	④ — 3.0	S.S. × 2.0	5–10 × 1.1
		Monel × 3.4	10–20 × 1.2
		S.S. clad × 1.5	20–30 × 1.4
		Monel × 2.1	30–40 × 1.6
		clad	40–50 × 1.8
			50–60 × 2.2

Temperature up to 300°C

Figure 6.6a, b. Horizontal pressure vessels. Time base mid-2004.  
 Purchase cost = (bare cost from figure) × Material factor × Pressure factor



Type	Material factors
① Sieve	C.S. × 1.0
② Valve	S.S. × 1.7
③ Bubble cap	

Figure 6.7a, b. Column plates. Time base mid-2004 (for column costs see Figure 6.4)  
 Installed cost = (cost from figure) × Material factor

Table 6.2. Purchase cost of miscellaneous equipment, cost factors for use in equation 6.7. Cost basis mid 2004

Equipment	Size unit, S	Size range	Constant C,£	Constant C,\$	Index n	Comment
<b>Agitators</b>						
Propeller	driver	5-75	1200	1900	0.5	
Turbine	power, kW		1800	3000	0.5	
<b>Boilers</b>						
Packaged						oil or gas fired
up to 10 bar	kg/h steam	$(5-50) \times 10^3$	70	120	0.8	
10 to 60 bar			60	100	0.8	
<b>Centrifuges</b>						
Horizontal basket	dia., m	0.5-1.0	35,000	58,000	1.3	carbon steel
Vertical basket			35,000	58,000	1.0	$\times 1.7$ for ss
<b>Compressors</b>						
Centrifugal	driver	20-500	1160	1920	0.8	electric,
	power, kW					max. press.
Reciprocating			1600	2700	0.8	50 bar
<b>Conveyors</b>						
Belt	length, m	2-40				
0.5 m wide			1200	1900	0.75	
1.0 m wide			1800	2900	0.75	
<b>Crushers</b>						
Cone	t/h	20-200	2300	3800	0.85	
Pulverisers	kg/h		2000	3400	0.35	
<b>Dryers</b>						
Rotary	area, m <sup>2</sup>	5-30	21,000	35,000	0.45	direct
Pan		2-10	4700	7700	0.35	gas fired
<b>Evaporators</b>						
Vertical tube	area, m <sup>2</sup>	10-100	12,000	20,000	0.53	carbon steel
Falling film			6500	10,000	0.52	
<b>Filters</b>						
Plate and frame	area, m <sup>2</sup>	5-50	5400	8800	0.6	cast iron
Vacuum drum		1-10	21,000	34,000	0.6	carbon steel
<b>Furnaces</b>						
Process						
Cylindrical	heat abs, kW	$10^3-10^4$	330	540	0.77	carbon steel
Box		$10^3-10^5$	340	560	0.77	$\times 2.0$ ss
<b>Reactors</b>						
Jacketed,	capacity, m <sup>3</sup>	3-30	9300	15,000	0.40	carbon steel
agitated			18,500	31,000	0.45	glass lined
<b>Tanks</b>						
Process	capacity, m <sup>3</sup>					
vertical		1-50	1450	2400	0.6	atmos. press.
horizontal		10-100	1750	2900	0.6	carbon steel
Storage						
floating roof		50-8000	2500	4350	0.55	$\times 2$ for
cone roof		50-8000	1400	2300	0.55	stainless

Table 6.3. Cost of column packing. Cost basis mid 2004

	Cost	£/m <sup>3</sup> (\$/m <sup>3</sup> )	
Size, mm	25	38	50
Saddles, stoneware	840 (1400)	620 (1020)	580 (960)
Pall rings, polypropylene	650 (1080)	400 (650)	250 (400)
Pall rings, stainless steel	1500 (2500)	1500 (2500)	830 (1360)

To use Table 6.2, substitute the values given for the particular type of equipment into the equation:

$$Ce = CS^n \quad (6.7)$$

where  $Ce$  = purchased equipment cost, £,

$S$  = characteristic size parameter, in the units given in Table 6.2,

$C$  = cost constant from Table 6.2,

$n$  = index for that type of equipment.

## 6.8. SUMMARY OF THE FACTORIAL METHOD

Many variations on the factorial method are used. The method outlined below can be used with the data given in this chapter to make a quick, approximate, estimate of the investment need for a project.

### **Procedure**

1. Prepare material and energy balances, draw up preliminary flow-sheets, size major equipment items and select materials of construction.
2. Estimate the purchase cost of the major equipment items. Use Figures 6.3 to 6.6 and Tables 6.2 and 6.3, or the general literature.
3. Calculate the total physical plant cost (PPC), using the factors given in Table 6.1

$$PPC = PCE(1 + f_1 + \dots + f_9) \quad (6.8)$$

4. Calculate the indirect costs from the direct costs using the factors given in Table 6.1.
5. The direct plus indirect costs give the total fixed capital.
6. Estimate the working capital as a percentage of the fixed capital; 10 to 20 per cent.
7. Add the fixed and working capital to get the total investment required.

## 6.9. OPERATING COSTS

An estimate of the operating costs, the cost of producing the product, is needed to judge the viability of a project, and to make choices between possible alternative processing schemes. These costs can be estimated from the flow-sheet, which gives the raw material and service requirements, and the capital cost estimate.

The cost of producing a chemical product will include the items listed below. They are divided into two groups.

1. Fixed operating costs: costs that do not vary with production rate. These are the bills that have to be paid whatever the quantity produced.
2. Variable operating costs: costs that are dependent on the amount of product produced.

### **Fixed costs**

1. Maintenance (labour and materials).
2. Operating labour.
3. Laboratory costs.
4. Supervision.
5. Plant overheads.

6. Capital charges.
7. Rates (and any other local taxes).
8. Insurance.
9. Licence fees and royalty payments.

### **Variable costs**

1. Raw materials.
2. Miscellaneous operating materials.
3. Utilities (Services).
4. Shipping and packaging.

The division into fixed and variable costs is somewhat arbitrary. Certain items can be classified without question, but the classification of other items will depend on the accounting practice of the particular organisation.

The items may also be classified differently in cost sheets and cost standards prepared to monitor the performance of the operating plant. For this purpose the fixed-cost items should be those over which the plant supervision has no control, and the variable items those for which they can be held accountable.

The costs listed above are the direct costs of producing the product at the plant site. In addition to these costs the site will have to carry its share of the Company's general operating expenses. These will include:

1. General overheads.
2. Research and development costs.
3. Sales expense.
4. Reserves.

How these costs are apportioned will depend on the Company's accounting methods. They would add about 20 to 30 per cent to direct production costs at the site.

### **6.9.1. Estimation of operating costs**

In this section the components of the fixed and variable costs are discussed and methods given for their estimation.

It is usually convenient to do the costing on an annual basis.

#### **Raw materials**

These are the major (essential) materials required to manufacture the product. The quantities can be obtained from the flow-sheet and multiplied by the operating hours per year to get the annual requirements.

The price of each material is best obtained by getting quotations from potential suppliers, but in the preliminary stages of a project prices can be taken from the literature.

The American journal *Chemical Marketing Reporter*, CMR (2004), publishes a weekly review of prices for most chemicals. The prices for a limited number of chemicals in Europe can be found in *European Chemical News*, ECN (2004). U.S. prices, converted to the local currency at the current rate of exchange, can be used as a guide to the probable price in other countries. An indication of the prices of a selected range of chemicals is given in Table 6.4 (see p. 263).

### ***Miscellaneous materials (plant supplies)***

Under this heading are included all the miscellaneous materials required to operate the plant that are not covered under the headings raw materials or maintenance materials.

Miscellaneous materials will include:

1. Safety clothing: hard hats, safety glasses etc.
2. Instrument charts and accessories
3. Pipe gaskets
4. Cleaning materials

An accurate estimate can be made by detailing and costing all the items needed, based on experience with similar plants. As a rough guide the cost of miscellaneous materials can be taken as 10 per cent of the total maintenance cost.

### ***Utilities (services)***

This term includes, power, steam, compressed air, cooling and process water, and effluent treatment; unless costed separately. The quantities required can be obtained from the energy balances and the flow-sheets. The prices should be taken from Company records, if available. They will depend on the primary energy sources and the plant location. The figures given in Table 6.5 can be used to make preliminary estimates. The current cost of utilities supplied by the utility companies: electricity, gas and water, can be obtained from their local area offices.

### ***Shipping and packaging***

This cost will depend on the nature of the product. For liquids collected at the site in the customer's own tankers the cost to the product would be small; whereas the cost of packaging and transporting synthetic fibres or polymers to a central distribution warehouse would add significantly to the product cost.

### ***Maintenance***

This item will include the cost of maintenance labour, which can be as high as the operating labour cost, and the materials (including equipment spares) needed for the maintenance of the plant. The annual maintenance costs for chemical plants are high, typically 5 to 15 per cent of the installed capital costs. They should be estimated from a knowledge of the maintenance costs on similar plant. As a first estimate the annual maintenance cost can be taken as 10 per cent of the fixed capital cost; the cost can be considered to be divided evenly between labour and materials.

### ***Operating labour***

This is the manpower needed to operate the plant: that directly involved with running the process.

The costs should be calculated from an estimate of the number of shift and day personnel needed, based on experience with similar processes. It should be remembered that to operate three shifts per day, at least five shift crews will be needed. The figures used for

Table 6.4. Raw material and product costs

Typical prices for bulk purchases, mid-1998. All deliveries by rail or road tanker, and all materials technical/industrial grade; unless otherwise stated

Chemical, and state	Cost unit	Cost £/unit	Cost \$/unit
Acetaldehyde, 99%	kg	0.53	0.48
Acetic acid	kg	0.60	1.10
Acetic anhydride	kg	0.70	1.15
Acetone	kg	0.63	1.03
Acrylonitrile	kg	1.20	1.90
Ally alcohol	kg	1.40	2.30
Ammonia, anhydrous	t	180	280
Ammonium nitrate, bulk	t	100	170
Ammonium sulphate, bulk	t	90	150
Amyl alcohol, mixed isomers	kg	0.67	1.20
Aniline	kg	0.52	0.84
Benzaldehyde, drums	kg	1.95	3.21
Benzene	kg	0.20	0.33
Benzoic acid, drums	kg	2.20	3.60
Butene-1	kg	0.30	0.40
n-Butyl alcohol	kg	0.75	1.30
n-Butyl ether, drums	kg	1.95	3.20
Calcium carbide, bulk	t	320	530
Calcium carbonate, bulk, coarse	t	105	145
Calcium chloride, bulk	t	200	275
Calcium hydroxide (lime), bulk	t	55	90
Carbon disulphide	t	370	500
Carbon tetrachloride, drums	kg	0.50	0.83
Chlorine	t	140	200
Chloroform	kg	0.45	0.70
Cupric chloride, anhydrous	kg	3.30	5.5
Dichlorobenzene	kg	0.95	1.54
Diethanolamine	kg	1.20	1.70
Ethanol, 90%	kg	4.20	6.50
Ethyl ether	kg	0.80	1.35
Ethylene, contract	kg	0.46	0.70
Ethylene glycol	kg	0.56	0.83
Ethylene oxide	kg	0.60	0.90
Formaldehyde, 37% w/w	kg	0.31	0.46
Formic acid, 94% w/w, drums	kg	0.63	1.05
Glycerine, 99.7%	kg	1.30	1.70
Heptane	kg	0.30	0.40
Hexane	kg	0.20	0.33
Hydrochloric acid, anhyd.	kg	1.00	1.70
Hydrochloric acid, 30% w/w	t	60	90
Hydrogen fluoride, anhydrous	kg	0.90	1.40
Hydrogen peroxide, 50% w/w	kg	0.50	0.80
Isobutanol, alcohol	kg	0.75	1.1
Isopropanol alcohol	kg	0.73	1.12
Maleic anhydride, drums	kg	1.80	2.90
Methanol	kg	0.63	1.00
Methyl ethyl ketone	kg	0.64	1.06
Monoethanolamine	kg	1.02	1.54
Methylstyrene	kg	0.70	1.15
Nitric acid, 50% w/w	t	130	220
98% w/w	t	220	370
Nitrobenzene	kg	0.47	0.78

*(continued overleaf)*



Table 6.4. (continued)

Chemical, and state	Cost unit	Cost £/unit	Cost \$/unit
Oxalic acid, sacks	kg	0.58	0.96
Phenol	kg	0.90	1.53
Phosgene, cyl.	kg	1.09	1.62
Phosphoric acid 75% w/w	kg	0.47	0.78
Potassium bicarbonate, sacks	kg	0.45	0.75
Potassium carbonate, sacks	kg	0.56	0.92
Potassium chloride	t	70	110
Potassium chromate, sacks	kg	0.80	1.30
Potassium hydroxide	kg	2.00	3.70
Potassium nitrate, bulk	t	350	570
Propylene	kg	0.43	0.64
Propylene oxide	kg	1.00	1.60
n-Propanol	kg	0.93	1.438
Sodium carbonate, sacks	kg	0.35	0.58
Sodium chloride, drums	kg	0.40	0.65
Sodium hydroxide, drums	kg	1.60	2.60
Sodium sulphate, bulk	t	72	120
Sodium thiosulphate	kg	0.38	0.57
Sulphur, crude, 99.5%, sacks	t	85	140
Sulphuric acid, 98% w/w	t	40	65
Titanium dioxide, sacks	kg	1.50	2.50
Toluene	kg	0.32	0.47
Toluene diisocyanate	kg	2.20	3.20
Trichloroethane	kg	0.56	0.94
Trichloroethylene	kg	0.84	1.40
Urea, 46% nitrogen, bulk	t	120	160
Vinyl acetate	kg	0.65	1.08
Vinyl chloride	kg	0.44	0.66
Xylenes	kg	0.29	0.43

Anhyd. = anhydrous, cyl. = cylinder, refin. = refined

Caution: Use these prices only as a rough guide to the probable price range. Actual prices at a given time will vary considerably from these values, depending on location, contract quantities, and the prevailing market forces.

Table 6.5. Cost of utilities, typical figures mid-2004

Utility	UK	USA
Mains water (process water)	60 p/t	50 c/t
Natural gas	0.4 p/MJ	0.7 c/MJ
Electricity	1.0 p/MJ	1.5 c/MJ
Fuel oil	65 £/t	100 \$/t
Cooling water (cooling towers)	1.5 p/t	1 c/t
Chilled water	5 p/t	8 c/t
Demineralised water	90 p/t	90 c/t
Steam (from direct fired boilers)	7 £/t	12 \$/t
Compressed air (9 bar)	0.4 p/m <sup>3</sup> (Stp)	0.6 c/m <sup>3</sup>
Instrument air (9 bar) (dry)	0.6 p/m <sup>3</sup> (Stp)	1 c/m <sup>3</sup>
Refrigeration	1.0 p/MJ	1.5 c/MJ
Nitrogen	6 p/m <sup>3</sup> (Stp)	8 c/m <sup>3</sup>

Note: £1 = 100p, 1\$ = 100c, 1 t = 1000 kg = 2200 ib, stp = 1 atm, 0°C

These prices should be used only as a rough guide to the likely cost of utilities. The cost of water will be very dependent on the plant location, and the price of all utilities will be determined by the current cost of energy.

the cost of each man should include an allowance for holidays, shift allowances, national insurance, pension contributions and any other overheads. The current wage rates per hour in the UK chemical industry (mid-2004) are £15–20, to which must be added up to 50 per cent for the various allowances and overheads mentioned above.

Chemical plants do not normally employ many people and the cost of operating labour would not normally exceed 15 per cent of the total operating cost. The direct overhead charges would add 20 to 30 per cent to this figure.

Wessel (1952) gives a method of estimating the number of man-hours required based on the plant capacity and the number of discrete operating steps.

### ***Supervision***

This heading covers the direct operating supervision: the management directly associated with running the plant. The number required will depend on the size of the plant and the nature of the process. The site would normally be broken down into a number of manageable units. A typical management team for a unit would consist of four to five shift foremen, a general foreman, and an area supervisor (manager) and his assistant. The cost of supervision should be calculated from an estimate of the total number required and the current salary levels, including the direct overhead costs. On average, one “supervisor” would be needed for each four to five operators. Typical salaries, mid-2004, are £20,000 to £45,000, depending on seniority. An idea of current salaries can be obtained from the salary reviews published periodically by the Institution of Chemical Engineers.

### ***Laboratory costs***

The annual cost of the laboratory analyses required for process monitoring and quality control is a significant item in most modern chemical plants. The costs should be calculated from an estimate of the number of analyses required and the standard charge for each analysis, based on experience with similar processes.

As a rough estimate the cost can be taken as 20 to 30 per cent of the operating labour cost, or 2 to 4 per cent of the total production cost.

### ***Plant overheads***

Included under this heading are all the general costs associated with operating the plant not included under the other headings; such as, general management, plant security, medical, canteen, general clerical staff and safety. It would also normally include the plant technical personnel not directly associated with and charged to a particular operating area. This group may be included in the cost of supervision, depending on the organisation’s practice.

The plant overhead cost is usually estimated from the total labour costs: operating, maintenance and supervision. A typical range would be 50 to 100 per cent of the labour costs; depending on the size of the plant and whether the plant was on a new site, or an extension of an existing site.

### ***Capital charges***

The investment required for the project is recovered as a charge on the project. How this charge is shown on an organisation’s books will depend on its accounting practices.

Capital is often recovered as a depreciation charge, which sets aside a given sum each year to repay the cost of the plant. If the plant is considered to “depreciate” at a fixed rate over its predicted operating life, the annual sum to be included in the operating cost can be easily calculated. The operating life of a chemical plant is usually taken as 10 years, which gives a depreciation rate of 10 per cent per annum. The plant is not necessarily replaced at the end of the depreciation period. The depreciation sum is really an internal transfer to the organisation’s fund for future investment. If the money for the investment is borrowed, the sum set aside would be used to repay the loan. Interest would also be payable on the loan at the current market rates. Normally the capital to finance a particular project is not taken as a direct loan from the market but comes from the company’s own reserves. Any interest charged would, like depreciation, be an internal (book) transfer of cash to reflect the cost of the capital used.

Rather than consider the cost of capital as depreciation or interest, or any other of the accounting terms used, which will depend on the accounting practice of the particular organisation and the current tax laws, it is easier to take the cost as a straight, unspecified, capital charge on the operating cost. This would be typically around 10 per cent of the fixed capital, annually, depending on the cost of money. As an approximate estimate the “capital charge” can be taken as 2 per cent above the current minimum lending rate. For a full discussion on the nature of depreciation and the cost of capital see Happle and Jordan (1975), Holland *et al.* (1983), Valle-Riestra (1983).

### ***Local taxes***

This term covers local taxes, which are calculated on the value of the site. A typical figure would be 1 to 2 per cent of the fixed capital.

### ***Insurance***

The cost of the site and plant insurance: the annual insurance premium paid to the insurers; usually about 1 to 2 per cent of the fixed capital.

### ***Royalties and licence fees***

If the process used has not been developed exclusively by the operating company, royalties and licence fees may be payable. These may be paid as a lump sum, included in the fixed capital, or as an annual fee; or payments based on the amount of product sold.

The cost would add about 1 per cent to 5 per cent to the sales price.

### ***Summary of production costs***

The various components of the operating costs are summarised in Table 6.6. The typical values given in this table can be used to make an approximate estimate of production costs.

Table 6.6. Summary of production costs

<i>Variable costs</i>	<i>Typical values</i>
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	.....
<i>Fixed costs</i>	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	.....
Direct production costs A + B	.....
13. Sales expense	20–30 per cent of the direct
14. General overheads	production cost
15. Research and development	
Sub-total C	.....
Annual production cost = A + B + C =	.....
Production cost £/kg =	$\frac{\text{Annual production cost}}{\text{Annual production rate}}$

### Example 6.4

Preliminary design work has been done on a process to recover a valuable product from an effluent gas stream. The gas will be scrubbed with a solvent in a packed column; the recovered product and solvent separated by distillation; and the solvent cooled and recycled. The major items of equipment that will be required are detailed below.

1. Absorption column: diameter 1 m, vessel overall height 15 m, packed height 12 m, packing 25 mm ceramic intalox saddles, vessel carbon steel, operating pressure 5 bar.
2. Recovery column: diameter 1 m, vessel overall height 20 m, 35 sieve plates, vessel and plates stainless steel, operating pressure 1 bar.
3. Reboiler: forced convection type, fixed tube sheets, area 18.6 m<sup>2</sup>, carbon steel shell, stainless-steel tubes, operating pressure 1 bar.
4. Condenser: fixed tube sheets, area 25.3 m<sup>2</sup>, carbon steel shell and tubes, operating pressure 1 bar.
5. Recycle solvent cooler: U-tubes, area 10.1 m<sup>2</sup>, carbon steel shell and tubes, operating pressure 5 bar.
6. Solvent and product storage tanks: cone roof, capacity 35 m<sup>3</sup>, carbon steel.

Estimated service requirements:

Steam	200 kg/h
Cooling water	5000 kg/h
Electrical power	100 kWh/d (360 MJ/d)

Estimated solvent loss 10 kg/d; price £400/t. Plant attainment 95 per cent.  
 Estimate the capital investment required for this project, and the annual operating cost;  
 date mid-2004.

## Solution

Purchased cost of major equipment items.

### *Absorption column*

Bare vessel cost (Figure 6.5a) £21,000; material factor 1.0, pressure factor 1.1

Vessel cost =  $21,000 \times 1.0 \times 1.1 = £23,000$

Packing cost (Table 6.3) £840/m<sup>3</sup>

Volume of packing =  $(\pi/4) \times 12 = 9.4 \text{ m}^3$

Cost of column packing =  $9.4 \times 840 = £7896$

Total cost of column  $21,000 + 7896 = 28,896$ , say £29,000

### *Recovery column*

Bare vessel cost (Figure 6.5a) £26,000; material factor 2.0, pressure factor 1.0

Vessel cost  $26,000 \times 2.0 \times 1.0 = £52,000$

Cost of a plate (Figure 6.7a), material factor 1.7 =  $200 \times 1.7 = £340$

Total cost of plates =  $35 \times 340 = £11,900$

Total cost of column =  $52,000 + 11,900 = 63,900$ , say £64,000

### *Reboiler*

Bare cost (Figure 6.3a) £11,000; type factor 0.8, pressure factor 1.0

Purchased cost =  $11,000 \times 0.8 \times 1.0 = £8800$

### *Condenser*

Bare cost (Figure 6.3a) £8500; type factor 0.8, pressure factor 1.0

Purchased cost =  $8500 \times 0.8 \times 1.0 = £6800$

### *Cooler*

Bare cost (Figure 6.3a) £4300; type factor 0.85, pressure factor 1.0

Purchased cost =  $4300 \times 0.85 \times 1.0 = £3700$

### *Solvent tank*

Purchase cost (Table 6.2) =  $1400 \times (35)^{0.55} = £9894$ , say £10,000

### *Product tank*

Purchase cost same as solvent tank = £10,000

Total purchase cost of major equipment items (PCE)

Absorption column	29,000
Recovery column	64,000
Reboiler	8000
Condenser	6000
Cooler	3000
Solvent tank	10,000
Product tank	10,000
Total	<u>£130,000</u>

Estimation of fixed capital cost, reference Table 6.1, fluids processing plant:

PCE £130,000	—
$f_1$ Equipment erection	0.40
$f_2$ Piping	0.70
$f_3$ Instrumentation	0.20
$f_4$ Electrical	0.10
$f_5$ Buildings	none required
$f_6$ Utilities	not applicable
$f_7$ Storages	provided in PCE
$f_8$ Site development	not applicable
$f_9$ Ancillary buildings	none required

Total physical plant cost (PPC) =  $132,300(1 + 0.4 + 0.7 + 0.2 + 0.1) = \underline{\underline{£317,520}}$

$f_{10}$  Design and Engineering 0.30

$f_{11}$  Contractor's Fee none (unlikely to be used for a small, plant project)

$f_{12}$  Contingencies 0.10

Fixed capital =  $317,520(1 + 0.3 + 0.1) = 44,528$  round up to £445,000

Working capital, allow 5% of fixed capital to cover the cost of the initial solvent charge =  $445,000 \times 0.05 = £22,250$ .

Total investment required for project =  $445,000 + 22,250 = 467,250$ , say £468,000

Annual operating costs, reference Table 6.6:

Operating time, allowing for plant attainment =  $365 \times 0.95 = 347$  d/y,  $347 \times 24 = 8328$  h/y.

**Variable costs:**

- Raw materials, solvent make-up =  $10 \times 347 \times 400/1000 =$  £ 1388
  - Miscellaneous materials, 10% of maintenance cost (item 5) = £ 2200
  - Utilities, cost from Table 6.5:
    - Steam, at  $7£/t = 7 \times 8328 \times 200/1000 =$  £11,659
    - Cooling water, at  $1.5$  p/t =  $(1.5/100) \times 8328 \times 5000/1000 =$  £ 625
    - Power, at  $1.2$  p/MJ =  $(1.2/100) \times 360 \times 347 =$  £ 1499
  - Shipping and packaging not applicable
- Variable costs = £17,371

**Fixed costs:**

5. Maintenance, take as 5% of fixed capital = $445,000 \times 0.05 =$	£22,250
6. Operating labour, allow one extra man on days. It is unlikely that one extra man per shift would be needed to operate this small plant, and one extra per shift would give a disproportionately high labour cost. Say, £30,000 per year, allowing for overheads =	£30,000
7. Supervision, no additional supervision would be needed	
8. Plant overheads, take as 50% of operating labour =	£15,000
9. Laboratory, take as 30% of operating labour =	£ 9000
10. Capital charges, 6% of fixed capital (bank rate 4%)	£26,700
11. Insurance, 1% of fixed capital	£ 4450
12. Local taxes	neglect
13. Royalties	not applicable
	Fixed cost = <u>£107,400</u>
Direct production costs = $17,396 + 107,400 =$	<u>£124,796</u>
14. Sales expense	not applicable
15. General overheads	not applicable
16. Research and development	not applicable
Annual operating cost, rounded =	<u>£125,000</u>

**6.10. ECONOMIC EVALUATION OF PROJECTS**

As the purpose of investing money in chemical plant is to earn money, some means of comparing the economic performance of projects is needed.

For small projects, and for simple choices between alternative processing schemes and equipment, the decisions can usually be made by comparing the capital and operating costs. More sophisticated evaluation techniques and economic criteria are needed when decisions have to be made between large, complex projects, particularly when the projects differ widely in scope, time scale and type of product. Some of the more commonly used techniques of economic evaluation and the criteria used to judge economic performance are outlined in this section. For a full discussion of the subject one of the many specialist texts that have been published should be consulted; Brennan (1998), Chauvel *et al.* (2003) and Vale-Riestra (1983). The booklet published by the Institution of Chemical Engineers, Allen (1991), is particularly recommended to students.

Making major investment decisions in the face of the uncertainties that will undoubtedly exist about plant performance, costs, the market, government policy, and the world economic situation, is a difficult and complex task (if not an impossible task) and in a large design organisation the evaluation would be done by a specialist group.

**6.10.1. Cash flow and cash-flow diagrams**

The flow of cash is the life blood of any commercial organisation. The cash flows in a manufacturing company can be likened to the material flows in a process plant.

The inputs are the cash needed to pay for research and development; plant design and construction; and plant operation. The outputs are goods for sale; and cash returns, are recycled, to the organisation from the profits earned. The “net cash flow” at any time is the difference between the earnings and expenditure. A cash-flow diagram, such as that shown in Figure 6.8, shows the forecast cumulative net cash flow over the life of a project. The cash flows are based on the best estimates of investment, operating costs, sales volume and sales price, that can be made for the project. A cash-flow diagram gives a clear picture of the resources required for a project and the timing of the earnings. The diagram can be divided into the following characteristic regions:

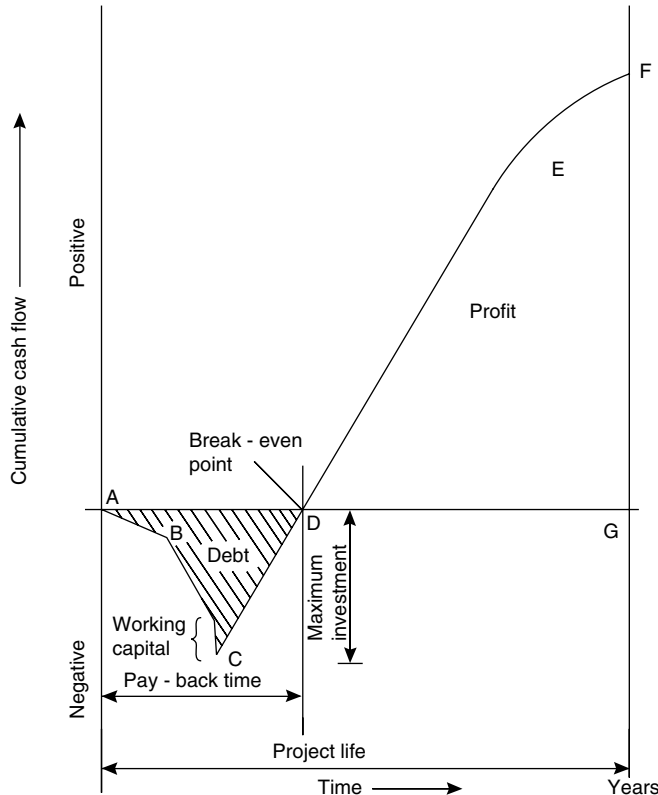


Figure 6.8. Project cash-flow diagram

- A–B The investment required to design the plant.
- B–C The heavy flow of capital to build the plant, and provide funds for start-up.
- C–D The cash-flow curve turns up at C, as the process comes on stream and income is generated from sales. The net cash flow is now positive but the cumulative amount remains negative until the investment is paid off, at point D. Point D is known as the *break-even point* and the time to reach the break-even point is called the *pay-back time*. In a different context, the term “break-even point” is used for the percentage of plant capacity at which the income equals the cost for production.



D–E In this region the cumulative cash flow is positive. The project is earning a return on the investment.

E–F Toward the end of project life the rate of cash flow may tend to fall off, due to increased operating costs and falling sale volume and price, and the slope of the curve changes.

The point F gives the final cumulative net cash flow at the end of the project life.

Net cash flow is a relatively simple and easily understood concept, and forms the basis for the calculation of other, more complex, measures of profitability.

### 6.10.2. Tax and depreciation

In calculating cash flows, as in Example 6.6, the project is usually considered as an isolated system, and taxes on profits and the effect of depreciation of the investment are not considered; tax rates are not constant and depend on government policy. In recent years, corporation (profits) tax has been running at around 30 per cent and this figure can be used to make an estimate of the cash flow after tax. Depreciation rates depend on government policy, and on the accounting practices of the particular company. At times, it has been government practice to allow higher depreciation rates for tax purposes in development areas; or to pay capital grants to encourage investment in these areas. The effect of government policy must clearly be taken into account at some stage when evaluating projects, particularly when considering projects in different countries.

### 6.10.3. Discounted cash flow (time value of money)

In Figure 6.8 the net cash flow is shown at its value in the year in which it occurred. So the figures on the ordinate show the “future worth” of the project: the cumulative “net future worth” (NFW).

The money earned in any year can be put to work (reinvested) as soon as it is available and start to earn a return. So money earned in the early years of the project is more valuable than that earned in later years. This “time value of money” can be allowed for by using a variation of the familiar compound interest formula. The net cash flow in each year of the project is brought to its “present worth” at the start of the project by discounting it at some chosen compound interest rate.

$$\text{Net present worth (NPW) of cash flow in year } n = \frac{\text{Estimated net cash flow in year } n \text{ (NFW)}}{(1+r)^n} \quad (6.9)$$

where  $r$  is the discount rate (interest rate) per cent/100 and

$$\text{Total NPW of project} = \sum_{n=1}^{n=t} \frac{\text{NFW}}{(1+r)^n} \quad (6.10)$$

$t$  = life of project, years.

The discount rate is chosen to reflect the earning power of money. It would be roughly equivalent to the current interest rate that the money could earn if invested.

The total NPW will be less than the total NFW, and reflects the time value of money and the pattern of earnings over the life of the project; see Example 6.6.

Most proprietary spreadsheets have procedures for calculating the cumulative NPW from a listing of the yearly net annual revenue (profit). Spreadsheets are useful tools for economic analysis and project evaluation.

#### 6.10.4. Rate of return calculations

Cash-flow figures do not show how well the capital invested is being used; two projects with widely different capital costs may give similar cumulative cash-flow figures. Some way of measuring the performance of the capital invested is needed. Rate of return (ROR), which is the ratio of annual profit to investment, is a simple index of the performance of the money invested. Though basically a simple concept, the calculation of the ROR is complicated by the fact that the annual profit (net cash flow) will not be constant over the life of the project. The simplest method is to base the ROR on the average income over the life of the project and the original investment.

$$\text{ROR} = \frac{\text{Cumulative net cash flow at end of project}}{\text{Life of project} \times \text{original investment}} \times 100 \text{ per cent} \quad (6.11)$$

From Figure 6.8.

$$\begin{aligned} \text{Cumulative income} &= F - C \\ \text{Investment} &= C \\ \text{Life of project} &= G \\ \text{then, ROR} &= \frac{F - C}{C \times G} \times 100 \text{ per cent} \end{aligned}$$

The rate of return is often calculated for the anticipated best year of the project: the year in which the net cash flow is greatest. It can also be based on the book value of the investment, the investment after allowing for depreciation. Simple rate of return calculations take no account of the time value of money.

#### 6.10.5. Discounted cash-flow rate of return (DCFRR)

Discounted cash-flow analysis, used to calculate the present worth of future earnings (Section 6.10.3), is sensitive to the interest rate assumed. By calculating the NPW for various interest rates, it is possible to find an interest rate at which the cumulative net present worth at the end of the project is zero. This particular rate is called the “discounted cash-flow rate of return” (DCFRR) and is a measure of the maximum rate that the project could pay and still break even by the end of the project life.

$$\sum_{n=1}^{n=t} \frac{\text{NFW}}{(1 + r')^n} = 0 \quad (6.12)$$

where  $r'$  = the discounted cash-flow rate of return (per cent/100),  
 NFW = the future worth of the net cash flow in year  $n$ ,  
 $t$  = the life of the project, years.

The value of  $r'$  is found by trial-and-error calculations. Finding the discount rate that just pays off the project investment over the project's life is analogous to paying off a mortgage. The more profitable the project, the higher the DCFRR that it can afford to pay.

DCFRR provides a useful way of comparing the performance of capital for different projects; independent of the amount of capital used and the life of the plant, or the actual interest rates prevailing at any time.

Other names for DCFRR are interest rate of return and internal rate of return.

#### **6.10.6. Pay-back time**

Pay-back time is the time required after the start of the project to pay off the initial investment from income; point D on Figure 6.7. Pay-back time is a useful criterion for judging projects that have a short life, or when the capital is only available for a short time.

It is often used to judge small improvement projects on operating plant. Typically, a pay-back time of 2 to 5 years would be expected from such projects.

Pay-back time as a criterion of investment performance does not, by definition, consider the performance of the project after the pay-back period.

#### **6.10.7. Allowing for inflation**

Inflation depreciates money in a manner similar to, but different from, the idea of discounting to allow for the time value of money. The effect of inflation on the net cash flow in future years can be allowed for in a similar manner to the net present worth calculation given by equation 6.9, using an inflation rate in place of, or added to, the discount rate  $r$ . However, the difficulty is to decide what the inflation rate is likely to be in future years. Also, inflation may well affect the sales price, operating costs and raw material prices differently. One approach is to argue that a decision between alternative projects made without formally considering the effect of inflation on future earnings will still be correct, as inflation is likely to affect the predictions made for both projects in a similar way.

#### **6.10.8. Sensitivity analysis**

The economic analysis of a project can only be based on the best estimates that can be made of the investment required and the cash flows. The actual cash flows achieved in any year will be affected by any changes in raw-materials costs, and other operating costs; and will be very dependent on the sales volume and price. A sensitivity analysis is a way of examining the effects of uncertainties in the forecasts on the viability of a project. To carry out the analysis the investment and cash flows are first calculated using what are considered the most probable values for the various factors; this establishes the base case for analysis. The cash flows, and whatever criteria of performance are to be used, are then calculated assuming a range of error for each of the factors in turn; for example, an error of, say,  $\pm 10$  per cent on the sales price might be assumed. This will show how sensitive the cash flows and economic criteria are to errors in the forecast figures. It gives some idea of the degree of risk involved in making judgements on the forecast performance of the project.

### 6.10.9. Summary

The investment criteria discussed in this section are set out in Table 6.7, which shows the main advantage and disadvantage of each criterion.

There is no one best criterion on which to judge an investment opportunity. A company will develop its own methods of economic evaluation, using the techniques discussed in this section, and will have a “target” figure of what to expect for the criterion used, based on their experience with previous successful, and unsuccessful, projects.

Table 6.7. Investment criteria

Criterion	Abbreviation	Units	Main advantage	Main shortcoming
Investment	—	£, \$	Shows financial resources needed	No indication of project performance
Net future worth	NFW	£, \$	Simple. When plotted as cash-flow diagram, shows timing of investment and income	Takes no account of the time value of money
Pay-back time	—	years	Shows how soon investment will be recovered	No information on later years
Net present worth	NPW	£, \$	As for NFW but accounts for timing of cash flows	Dependent on discount rate used
Rate of return	ROR	%	Measures performance of capital	Takes no account of timing of cash flows Dependent on definition of income (profit) and investment
Discounted cash-flow rate of return	DCFRR	%	Measures performance of capital allowing for timing of cash flows	No indication of the resources needed

A figure of 20 to 30 per cent for the return on investment (ROR) can be used as a rough guide for judging small projects, and when decisions have to be made on whether to install additional equipment to reduce operating costs. This is equivalent to saying that for a project to be viable the investment needed should not be greater than about 4 to 5 times the annual savings achieved.

As well as economic performance, many other factors have to be considered when evaluating projects; such as those listed below:

1. Safety.
2. Environmental problems (waste disposal).
3. Political considerations (government policies).
4. Location of customers.
5. Availability of labour.
6. Availability of supporting services.
7. Company experience in the particular technology.

### Example 6.5

A plant is producing 10,000 t/y of a product. The overall yield is 70 per cent, on a mass basis (kg of product per kg raw material). The raw material costs £10/t, and the product

sells for £35/t. A process modification has been devised that will increase the yield to 75 per cent. The additional investment required is £35,000, and the additional operating costs are negligible. Is the modification worth making?

### Solution

There are two ways of looking at the earnings to be gained from the modification:

1. If the additional production given by the yield increase can be sold at the current price, the earnings on each additional ton of production will equal the sales price less the raw material cost.
2. If the additional production cannot be readily sold, the modification results in a reduction in raw material requirements, rather than increased sales, and the earnings (savings) are from the reduction in annual raw material costs.

The second way gives the lowest figures and is the safest basis for making the evaluation. At 10,000 t/y production

$$\text{Raw material requirements at 70 per cent yield} = \frac{10,000}{0.7} = 14,286$$

$$\text{at 75 per cent yield} = \frac{10,000}{0.75} = \underline{13,333}$$

savings 953 t/y

$$\text{Cost savings, at } \pounds 10/t, = 953 \times 10 = \pounds 9530 \text{ per year}$$

$$\text{ROR} = \frac{9530}{35,000} \times 100 = \underline{\underline{27 \text{ per cent}}}$$

Pay-back time (as the annual savings are constant, the pay-back time will be the reciprocal of the ROR)

$$= \frac{100}{27} = \underline{\underline{3.7 \text{ years}}}$$

On these figures the modification would be considered worthwhile.

### Example 6.6

It is proposed to build a plant to produce a new product. The estimated investment required is 12.5 million pounds and the timing of the investment will be:

year 1	1.0 million (design costs)
year 2	5.0 million (construction costs)
year 3	5.0 million " "
year 4	1.5 million (working capital)

The plant will start up in year 4.

The forecast sales price, sales volume, and raw material costs are shown in Table 6.8.

Table 6.8. Summary of data and results for example 6.6

End of year				During year		At year end	At commencement of project				
	Forecast sales 10 <sup>3</sup> t	Forecast selling Price £/t	Raw material costs £/t product	Sale income less operating costs 10 <sup>6</sup> £	Net cash flow 10 <sup>6</sup> £	Cumulative cash flow 10 <sup>6</sup> £ (Project NFW)	Discounted cash flow at 15 per cent 10 <sup>6</sup> £	Cumulative DCF (Project NPW) 10 <sup>6</sup> £	Project NPW at 25 per cent discount rate	Project NPW at 35 per cent discount rate	Project NPW at 37 per cent discount rate
1	0	—	—	0	-1.0	-1.00	-0.87	-0.87	-0.80	-0.74	0.73
2	0	—	—	0	-5.0	-6.00	-3.78	-4.65	-4.00	-3.48	-3.39
3	0	—	—	0	-5.0	-11.00	-3.29	-7.94	-6.56	-5.52	-5.34
4	100	150	90	4.6	3.10	-7.90	1.77	-6.17	-5.29	-4.58	-4.46
5	105	150	90	4.85	4.85	-3.05	2.41	-4.03	-3.70	-3.50	-3.45
6	110	150	90	5.10	5.10	2.05	2.20	-1.83	-2.36	-2.66	-2.68
7	120	150	90	5.60	5.60	7.65	2.11	0.28	-1.19	-1.97	-2.06
8	130	150	90	6.10	6.10	13.75	1.99	2.27	-0.17	-1.42	-1.57
9	140	150	90	6.50	6.50	20.25	1.85	4.12	0.70	-0.98	-1.19
10	150	145	85	7.00	7.00	27.25	1.73	5.85	1.45	-0.64	-0.89
11	165	140	85	6.93	6.93	34.18	1.49	7.34	2.05	-0.38	-0.67
12	180	140	85	7.60	7.60	41.78	1.42	8.76	2.57	-0.17	-0.50
13	190	140	85	8.05	8.05	49.83	1.31	10.07	3.01	-0.01	-0.36
14	200	135	80	8.05	8.05	57.88	1.14	11.21	3.36	0.11	-0.27
15	190	130	75	7.62	7.62	65.50	0.94	12.15	3.63	0.19	-0.20
16	180	120	75	7.19	7.19	72.69	0.77	12.92	3.83	0.25	-0.15
17	170	115	70	5.06	5.06	77.75	0.47	13.39	3.95	0.28	-0.13
18	160	110	70	3.93	3.93	81.68	0.32	13.71	4.02	0.30	-0.12
19	150	100	70	2.15	2.15	83.83	0.15	13.86	4.05	0.31	-0.11

The fixed operating costs are estimated to be:

£400,000 per year up to year 9  
£500,000 per year from year 9 to 13  
£550,000 per year from year 13

The variable operating costs are estimated to be:

£10 per ton of product up to year 13  
£13 per ton of product from year 13

Calculate:

1. The net cash flow in each year.
2. The future worth of the project, NFW.
3. The present worth, NPW, at a discount rate of 15 per cent.
4. The discounted cash-flow rate of return, DCFRR.
5. The pay-back time.

No account needs to be taken of tax in this exercise; or the scrap value of the equipment and value of the site at the end of the project life. For the discounting calculation, cash flows can be assumed to occur at the end of the year in which they actually occur.

## Solution

The cash-flow calculations are summarised in Table 6.8. Sample calculations to illustrate the methods used are given below.

### For year 4

Investment (negative cash flow)	=	$£1.5 \times 10^6$
Sales income = $100 \times 10^3 \times 150$	=	$£15.0 \times 10^6$
Raw material costs = $100 \times 10^3 \times 90$	=	$£9.0 \times 10^6$
Fixed operating costs	=	$£0.4 \times 10^6$
Variable operating costs = $100 \times 10^3 \times 10$	=	$£1.0 \times 10^6$
Net cash flow = sales income – costs – investment		
	=	$15.0 - 10.4 - 1.5 = 3.1$ million pounds
Discounted cash flow (at 15 per cent) = $\frac{3.1}{(1 + 0.15)^4}$	=	$£1.77 \times 10^6$

### For year 8

Investment		nil
Sales income = $130 \times 10^3 \times 150$	=	$£19.5 \times 10^6$
Raw material costs = $130 \times 10^3 \times 90$	=	$£11.7 \times 10^6$
Fixed operating costs	=	$£0.4 \times 10^6$
Variable operating costs = $130 \times 10^3 \times 10$	=	$£1.3 \times 10^6$
Net cash flow = $19.5 - 13.4 = 6.10$ million pounds		
DCF = $\frac{6.1}{(1.15)^8}$	=	1.99

### DCFRR

This is found by trial-and-error calculations. The present worth has been calculated at discount rates of 25, 35 and 37 per cent. From the results shown in Table 6.8 it will be seen that the rate to give zero present worth will be around 36 per cent. This is the discounted cash-flow rate of return for the project.

## 6.11. COMPUTER METHODS FOR COSTING AND PROJECT EVALUATION

Most large manufacturing and contracting organisations use computer programs to aid in the preparation of cost estimates and in process evaluation. Many have developed their own programs, using cost data available from company records to ensure that the estimates are reliable. Of the packages available commercially, QUESTIMATE, marketed by the Icarus Corporation, is probably the most widely used.

Costing and economic evaluation programs also form part of some of the commercial process design packages; such as the ICARUS program which is available from Aspen Tech, see Chapter 4, Table 4.1.

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## 6.13. NOMENCLATURE

		Dimensions in MT £ or \$
<i>A</i>	Year in which cost is known (equation 6.1)	<b>T</b>
<i>B</i>	Year in which cost is to be estimated (equation 6.1)	<b>T</b>
<i>C</i>	Cost constant in equation 6.7	*
<i>C<sub>e</sub></i>	Purchased equipment cost	£ or \$
<i>C<sub>f</sub></i>	Fixed capital cost	£ or \$
<i>C<sub>1</sub></i>	Capital cost of plant 1	£ or \$
<i>C<sub>2</sub></i>	Capital cost of plant 2	£ or \$
<i>f<sub>L</sub></i>	Lang factors (equation 6.3)	—
<i>f<sub>1</sub> ... f<sub>9</sub></i>	Capital cost factors (Table 6.1)	—
<i>N</i>	Number of significant processing steps	—
<i>n</i>	Capital cost index in equation 6.4	—
<i>Q</i>	Plant capacity	<b>MT<sup>-1</sup></b>
<i>S</i>	Equipment size unit in equation 6.4	*



$S_1$	Capacity of plant 1	$MT^{-1}$
$S_2$	Capacity of plant 2	$MT^{-1}$
$s$	Reactor conversion	—

Asterisk (\*) indicates that these dimensions are dependent on the type of equipment.

## 6.14. PROBLEMS

- 6.1.** The capital cost of a plant to produce 100 t per day of aniline was 8.5 million US dollars in mid-1992. Estimate the cost in pounds sterling in January 2004. Take the exchange rates as: £1 = \$2.0 in mid-1992 and £1 = \$1.8 in January 2004.
- 6.2.** The process used in the manufacture of aniline from nitrobenzene is described in Appendix G, design problem G.8. The process involves six significant stages:  
 Vaporisation of the nitrobenzene  
 Hydrogenation of the nitrobenzene  
 Separation of the reactor products by condensation  
 Recovery of crude aniline by distillation  
 Purification of the crude nitrobenzene  
 Recovery of aniline from waste water streams
- Estimate the capital cost of a plant to produce 20,000 tonne per year.
- 6.3.** A reactor vessel cost £365,000 in June 1998, estimate the cost in mid-2004.
- 6.4.** The cost of a distillation column was \$225,000 in early 1998, estimate the cost in January 2004.
- 6.5.** Using the data on equipment costs given in this chapter, estimate the cost of the following equipment:
1. A shell and tube heat exchanger, heat transfer area 50 m<sup>2</sup>, floating head type, carbon steel shell, stainless steel tubes, operating pressure 25 bar.
  2. A kettle reboiler: heat transfer area 25 m<sup>2</sup>, carbon steel shell and tubes, operating pressure 10 bar.
  3. A horizontal, cylindrical, storage tank, 3 m diameter, 12 m long, used for liquid chlorine at 10 bar, material carbon steel.
  4. A plate column: diameter 2 m height 25 m, stainless clad vessel, 20 stainless steel sieve plates, operating pressure 5 bar.
- 6.6.** Compare the cost the following types of heat exchangers, to give a heat transfer area of 10 m<sup>2</sup>. Take the construction material as carbon steel.
1. Shell and tube, fixed head
  2. Double-pipe
- 6.7.** Estimate the cost of the following items of equipment:
1. A packaged boiler to produce 20,000 kg/h of steam at 10 bar.
  2. A centrifugal compressor, driver power 75 kW
  3. A plate and frame filter press, filtration area 10 m<sup>2</sup>

4. A floating roof storage tank, capacity 50,000 m<sup>3</sup>
  5. A cone roof storage tank, capacity 35,000 m<sup>3</sup>
- 6.8.** A storage tank is purged continuously with a stream of nitrogen. The purge stream leaving the tank is saturated with the product stored in the tank. A major part of the product lost in the purge could be recovered by installing a scrubbing tower to absorb the product in a solvent. The solution from the tower could be fed to a stage in the production process, and the product and solvent recovered without significant additional cost. A preliminary design of the purge recovery system has been made. It would consist of:
1. A small tower 0.5 m diameter, 4 m high, packed with 25 mm ceramic saddles, packed height 3 m.
  2. A small storage tank for the solution, 5 m<sup>3</sup> capacity.
  3. The necessary pipe work, pump, and instrumentation.

All materials of construction, carbon steel.

Using the following data, evaluate whether it would be economical to install the recovery system:

1. cost of product £5 per kg,
2. cost of solvent 20 p/kg,
3. additional solvent make-up 10 kg/d,
4. current loss of product 0.7 kg/h,
5. anticipated recovery of product 80 per cent,
6. additional service(utility) costs, negligible.

Other operating costs will be insignificant.

- 6.9.** Make a rough estimate of the cost of steam per ton, produced from a packaged boiler. 10,000 kg per hour of steam are required at 15 bar. Natural gas will be used as the fuel, calorific value 39 MJ/m<sup>3</sup>. Take the boiler efficiency as 80 per cent. No condensate will be returned to the boiler.
- 6.10.** The production of methyl ethyl ketone (MEK) is described in Appendix G, problem G.3. A preliminary design has been made for a plant to produce 10,000 tonne per year. The major equipment items required are listed below. The plant attainment will be 8000 hours per year. Estimate the capital required for this project, and the production cost. The plant will be built on an existing site with adequate resources to provide the ancillary requirements of the new plant.

*Major equipment items*

1. Butanol vaporiser: shell and tube heat exchanger, kettle type, heat transfer area 15 m<sup>2</sup>, design pressure 5 bar, materials carbon steel.
2. Reactor feed heaters, two off: shell and tube, fixed head, heat transfer area 25 m<sup>2</sup>, design pressure 5 bar, materials stainless steel.
3. Reactor, three off: shell and tube construction, fixed tube sheets, heat transfer area 50 m<sup>2</sup>, design pressure 5 bar, materials stainless steel.

4. Condenser: shell and tube heat exchanger, fixed tube sheets, heat transfer area 25 m<sup>2</sup>, design pressure 2 bar, materials stainless steel.
5. Absorption column: packed column, diameter 0.5 m, height 6.0 m, packing height 4.5 m, packing 25 mm ceramic saddles, design pressure 2 bar, material carbon steel.
6. Extraction column: packed column, diameter 0.5 m, height 4 m, packed height 3 m, packing 25 mm stainless steel pall rings, design pressure 2 bar, material carbon steel.
7. Solvent recovery column: plate column, diameter 0.6 m, height 6 m, 10 stainless steel sieve plates, design pressure 2 bar, column material carbon steel.
8. Recover column reboiler: thermosyphon, shell and tube, fixed tube sheets, heat transfer area 4 m<sup>2</sup>, design pressure 2 bar, materials carbon steel.
9. Recovery column condenser: double-pipe, heat transfer area 1.5 m<sup>2</sup>, design pressure 2 bar, materials carbon steel.
10. Solvent cooler: double pipe exchanger, heat transfer area 2 m<sup>2</sup>, materials stainless steel.
11. Product purification column: plate column, diameter 1 m<sup>2</sup>, height 20 m, 15 sieve plates, design pressure 2 bar, materials stainless steel.
12. Product column reboiler: kettle type, heat transfer area 4 m<sup>2</sup>, design pressure 2 bar, materials stainless steel.
13. Product column condenser: shell and tube, floating head, heat transfer area 15 m<sup>2</sup>, design pressure 2 bar, materials stainless steel.
14. Feed compressor: centrifugal, rating 750 kW.
15. Butanol storage tank: cone roof, capacity 400 m<sup>3</sup>, material carbon steel.
16. Solvent storage tank: horizontal, diameter 1.5 m, length 5 m, material carbon steel.
17. Product storage tank: cone roof, capacity 400 m<sup>3</sup>, material carbon steel.

#### *Raw materials*

1. 2-butanol, 1.045 kg per kg of MEK, price £450/t (\$750/t).
2. Solvent (trichloroethane) make-up 7000 kg per year, price 60p/kg. (\$1.0/kg).

#### *Utilities*

Fuel oil, 3000 t per year  
 Cooling water, 120 t/hour  
 Steam, low pressure, 1.2 t/h  
 Electrical power, 1 MW

The fuel oil is burnt to provide flue gases for heating the reactor feed and the reactor. The cost of the burner need not be included in this estimate. Some of the fuel requirements could be provided by using the by-product hydrogen. Also, the exhaust flue gases could be used to generate steam. The economics of these possibilities need not be considered.

- 6.11.** A plant is proposing to install a combined heat and power system to supply electrical power and process steam. Power is currently taken from a utility company and steam is generated using on-site boilers.

The capital cost of the CHP plant is estimated to be £3 million pounds (5 million dollars). Combined heat and power is expected to give net savings of £700,000 (\$1,150,000) per year. The plant is expected to operate for 10 years after the completion of construction.

Calculate the cumulative net present worth of the project, at a discount rate of 8 per cent. Also, calculate the discounted cash flow rate of return.

Construction will take two years, and the capital will be paid in two equal increments, at the end of the first and second year. The savings (income) can be taken as paid at the end of each year. Production will start on the completion of construction.

## CHAPTER 7

# *Materials of Construction*

### 7.1. INTRODUCTION

This chapter covers the selection of materials of construction for process equipment and piping.

Many factors have to be considered when selecting engineering materials, but for chemical process plant the overriding consideration is usually the ability to resist corrosion. The process designer will be responsible for recommending materials that will be suitable for the process conditions. He must also consider the requirements of the mechanical design engineer; the material selected must have sufficient strength and be easily worked. The most economical material that satisfies both process and mechanical requirements should be selected; this will be the material that gives the lowest cost over the working life of the plant, allowing for maintenance and replacement. Other factors, such as product contamination and process safety, must also be considered. The mechanical properties that are important in the selection of materials are discussed briefly in this chapter. Several books have been published on the properties of materials, and the metal-working processes used in equipment fabrication, and a selection suitable for further study is given in the list of references at the end of this chapter. The mechanical design of process equipment is discussed in Chapter 13.

A detailed discussion of the theoretical aspects of corrosion is not given in this chapter, as this subject is covered comprehensively in several books: Revie (2002), Fontana (1986), Dillon (1986) and Schweitzer (1989).

Corrosion and corrosion prevention are also the subject of one of the design guides published by the Design Council, Ross (1977).

### 7.2. MATERIAL PROPERTIES

The most important characteristics to be considered when selecting a material of construction are:

1. Mechanical properties
  - (a) Strength—tensile strength
  - (b) Stiffness—elastic modulus (Young's modulus)
  - (c) Toughness—fracture resistance
  - (d) Hardness—wear resistance
  - (e) Fatigue resistance
  - (f) Creep resistance
2. The effect of high and low temperatures on the mechanical properties

3. Corrosion resistance
4. Any special properties required; such as, thermal conductivity, electrical resistance, magnetic properties
5. Ease of fabrication—forming, welding, casting (see Table 7.1)
6. Availability in standard sizes—plates, sections, tubes
7. Cost

Table 7.1. A guide to the fabrication properties of common metals and alloys

	Machining	Cold working	Hot working	Casting	Welding	Annealing temp. °C
Mild steel	S	S	S	D	S	750
Low alloy steel	S	D	S	D	S	750
Cast iron	S	U	U	S	D/U	—
Stainless steel (18Cr, 8Ni)	S	S	S	D	S	1050
Nickel	S	S	S	S	S	1150
Monel	S	S	S	S	S	1100
Copper (deoxidised)	D	S	S	S	D	800
Brass	S	D	S	S	S	700
Aluminium	S	S	S	D	S	550
Dural	S	S	S	—	S	350
Lead	—	S	—	—	S	—
Titanium	S	S	U	U	D	—

S—Satisfactory, D—Difficult, special techniques needed.  
U—Unsatisfactory.

## 7.3. MECHANICAL PROPERTIES

Typical values of the mechanical properties of the more common materials used in the construction of chemical process equipment are given in Table 7.2.

### 7.3.1. Tensile strength

The tensile strength (tensile stress) is a measure of the basic strength of a material. It is the maximum stress that the material will withstand, measured by a standard tensile test. The older name for this property, which is more descriptive of the property, was Ultimate Tensile Strength (UTS).

The design stress for a material, the value used in any design calculations, is based on the tensile strength, or on the yield or proof stress (see Chapter 13).

Proof stress is the stress to cause a specified permanent extension, usually 0.1 per cent.

### 7.3.2. Stiffness

Stiffness is the ability to resist bending and buckling. It is a function of the elastic modulus of the material and the shape of the cross-section of the member (the second moment of area).

Table 7.2. Mechanical properties of common metals and alloys (typical values at room temperature)

	Tensile strength (N/mm <sup>2</sup> )	0.1 per cent proof stress (N/mm <sup>2</sup> )	Modulus of elasticity (kN/mm <sup>2</sup> )	Hardness Brinell	Specific gravity
Mild steel	430	220	210	100–200	7.9
Low alloy steel	420–660	230–460	210	130–200	7.9
Cast iron	140–170	—	140	150–250	7.2
Stainless steel (18Cr, 8Ni)	>540	200	210	160	8.0
Nickel (>99 per cent Ni)	500	130	210	80–150	8.9
Monel	650	170	170	120–250	8.8
Copper (deoxidised)	200	60	110	30–100	8.9
Brass (Admiralty)	400–600	130	115	100–200	8.6
Aluminium (>99 per cent)	80–150	—	70	30	2.7
Dural	400	150	70	100	2.7
Lead	30	—	15	5	11.3
Titanium	500	350	110	150	4.5

### 7.3.3. Toughness

Toughness is associated with tensile strength, and is a measure of the material's resistance to crack propagation. The crystal structure of ductile materials, such as steel, aluminium and copper, is such that they stop the propagation of a crack by local yielding at the crack tip. In other materials, such as the cast irons and glass, the structure is such that local yielding does not occur and the materials are brittle. Brittle materials are weak in tension but strong in compression. Under compression any incipient cracks present are closed up. Various techniques have been developed to allow the use of brittle materials in situations where tensile stress would normally occur. For example, the use of prestressed concrete, and glass-fibre-reinforced plastics in pressure vessels construction.

A detailed discussion of the factors that determine the fracture toughness of materials can be found in the books by Institute of Metallurgists (1960) and Boyd (1970). Gordon (1976) gives an elementary, but very readable, account of the strength of materials in terms of their macroscopic and microscopic structure.

### 7.3.4. Hardness

The surface hardness, as measured in a standard test, is an indication of a material's ability to resist wear. This will be an important property if the equipment is being designed to handle abrasive solids, or liquids containing suspended solids which are likely to cause erosion.

### 7.3.5. Fatigue

Fatigue failure is likely to occur in equipment subject to cyclic loading; for example, rotating equipment, such as pumps and compressors, and equipment subjected to pressure cycling. A comprehensive treatment of this subject is given by Harris (1976).

### 7.3.6. Creep

Creep is the gradual extension of a material under a steady tensile stress, over a prolonged period of time. It is usually only important at high temperatures; for instance, with steam and gas turbine blades. For a few materials, notably lead, the rate of creep is significant at moderate temperatures. Lead will creep under its own weight at room temperature and lead linings must be supported at frequent intervals.

The creep strength of a material is usually reported as the stress to cause rupture in 100,000 hours, at the test temperature.

### 7.3.7. Effect of temperature on the mechanical properties

The tensile strength and elastic modulus of metals decrease with increasing temperature. For example, the tensile strength of mild steel (low carbon steel,  $C < 0.25$  per cent) is  $450 \text{ N/mm}^2$  at  $25^\circ\text{C}$  falling to 210 at  $500^\circ\text{C}$ , and the value of Young's modulus  $200,000 \text{ N/mm}^2$  at  $25^\circ\text{C}$  falling to  $150,000 \text{ N/mm}^2$  at  $500^\circ\text{C}$ . If equipment is being designed to operate at high temperatures, materials that retain their strength must be selected. The stainless steels are superior in this respect to plain carbon steels.

Creep resistance will be important if the material is subjected to high stresses at elevated temperatures. Special alloys, such as Inconel (International Nickel Co.), are used for high temperature equipment such as furnace tubes.

The selection of materials for high-temperature applications is discussed by Day (1979).

At low temperatures, less than  $10^\circ\text{C}$ , metals that are normally ductile can fail in a brittle manner. Serious disasters have occurred through the failure of welded carbon steel vessels at low temperatures. The phenomenon of brittle failure is associated with the crystalline structure of metals. Metals with a body-centred-cubic (bcc) lattice are more liable to brittle failure than those with a face-centred-cubic (fcc) or hexagonal lattice. For low-temperature equipment, such as cryogenic plant and liquefied-gas storages, austenitic stainless steel (fcc) or aluminium alloys (hex) should be specified; see Wigley (1978).

V-notch impact tests, such as the Charpy test, are used to test the susceptibility of materials to brittle failure: see Wells (1968) and BS 131.

The brittle fracture of welded structures is a complex phenomenon and is dependent on plate thickness and the residual stresses present after fabrication; as well as the operating temperature. A comprehensive discussion of brittle fracture in steel structures is given by Boyd (1970).

## 7.4. CORROSION RESISTANCE

The conditions that cause corrosion can arise in a variety of ways. For this brief discussion on the selection of materials it is convenient to classify corrosion into the following categories:

1. General wastage of material—uniform corrosion.
2. Galvanic corrosion—dissimilar metals in contact.
3. Pitting—localised attack.
4. Intergranular corrosion.



5. Stress corrosion.
6. Erosion–corrosion.
7. Corrosion fatigue.
8. High temperature oxidation.
9. Hydrogen embrittlement.

Metallic corrosion is essentially an electrochemical process. Four components are necessary to set up an electrochemical cell:

1. Anode—the corroding electrode.
2. Cathode—the passive, non-corroding electrode.
3. The conducting medium—the electrolyte—the corroding fluid.
4. Completion of the electrical circuit—through the material.

Cathodic areas can arise in many ways:

- (i) Dissimilar metals.
- (ii) Corrosion products.
- (iii) Inclusions in the metal, such as slag.
- (iv) Less well-aerated areas.
- (v) Areas of differential concentration.
- (vi) Differentially strained areas.

#### 7.4.1. Uniform corrosion

This term describes the more or less uniform wastage of material by corrosion, with no pitting or other forms of local attack. If the corrosion of a material can be considered to be uniform the life of the material in service can be predicted from experimentally determined corrosion rates.

Corrosion rates are usually expressed as a penetration rate in inches per year, or mills per year (mpy) (where a mill =  $10^{-3}$  inches). They are also expressed as a weight loss in milligrams per square decimetre per day (mdd). In corrosion testing, the corrosion rate is measured by the reduction in weight of a specimen of known area over a fixed period of time.

$$\text{ipy} = \frac{12w}{tA\rho} \quad (7.1)$$

where  $w$  = mass loss in time  $t$ , lb,

$t$  = time, years,

$A$  = surface area, ft<sup>2</sup>,

$\rho$  = density of material, lb/ft<sup>3</sup>,

as most of the published data on corrosion rates are in imperial units.

In SI units 1 ipy = 25 mm per year.

When judging corrosion rates expressed in mdd it must be remembered that the penetration rate depends on the density of the material. For ferrous metals 100 mdd = 0.02 ipy.

What can be considered as an acceptable rate of attack will depend on the cost of the material; the duty, particularly as regards to safety; and the economic life of the plant. For

the more commonly used inexpensive materials, such as the carbon and low alloy steels, a guide to what is considered acceptable is given in Table 7.3. For the more expensive alloys, such as the high alloy steels, the brasses and aluminium, the figures given in Table 7.3 should be divided by 2.

Table 7.3. Acceptable corrosion rates

	Corrosion rate	
	ipy	mm/y
Completely satisfactory	<0.01	0.25
Use with caution	<0.03	0.75
Use only for short exposures	<0.06	1.5
Completely unsatisfactory	>0.06	1.5

The corrosion rate will be dependent on the temperature and concentration of the corrosive fluid. An increase in temperature usually results in an increased rate of corrosion; though not always. The rate will depend on other factors that are affected by temperature, such as oxygen solubility.

The effect of concentration can also be complex. For example, the corrosion of mild steel in sulphuric acid, where the rate is unacceptably high in dilute acid and at concentrations above 70 per cent, but is acceptable at intermediate concentrations.

#### 7.4.2. Galvanic corrosion

If dissimilar metals are placed in contact, in an electrolyte, the corrosion rate of the anodic metal will be increased, as the metal lower in the electrochemical series will readily act as a cathode. The galvanic series in sea water for some of the more commonly used metals is shown in Table 7.4. Some metals under certain conditions form a natural protective film; for example, stainless steel in oxidising environments. This state is denoted by "passive" in the series shown in Table 7.4; active indicates the absence of the protective film. Minor

Table 7.4. Galvanic series in sea water

Noble end (protected end)	18/8 stainless steel (passive)
	Monel
	Inconel (passive)
	Nickel (passive)
	Copper
	Aluminium bronze (Cu 92 per cent, Al 8 per cent)
	Admiralty brass (Cu 71 per cent, Zn 28 per cent, Sn 1 per cent)
	Nickel (active)
	Inconel (active)
	Lead
	18/8 stainless steel (active)
	Cast iron
	Mild steel
	Aluminium
	Galvanised steel
	Zinc
	Magnesium

shifts in position in the series can be expected in other electrolytes, but the series for sea water is a good indication of the combinations of metals to be avoided. If metals which are widely separated in the galvanic series have to be used together, they should be insulated from each other, breaking the conducting circuit. Alternatively, if sacrificial loss of the anodic material can be accepted, the thickness of this material can be increased to allow for the increased rate of corrosion. The corrosion rate will depend on the relative areas of the anodic and cathodic metals. A high cathode to anode area should be avoided. Sacrificial anodes are used to protect underground steel pipes.

### 7.4.3. Pitting

Pitting is the term given to very localised corrosion that forms pits in the metal surface. If a material is liable to pitting penetration can occur prematurely and corrosion rate data are not a reliable guide to the equipment life.

Pitting can be caused by a variety of circumstances; any situation that causes a localised increase in corrosion rate may result in the formation of a pit. In an aerated medium the oxygen concentration will be lower at the bottom of a pit, and the bottom will be anodic to the surrounding metal, causing increased corrosion and deepening of the pit. A good surface finish will reduce this type of attack. Pitting can also occur if the composition of the metal is not uniform; for example, the presence of slag inclusions in welds. The impingement of bubbles can also cause pitting, the effect of cavitation in pumps, which is an example of erosion-corrosion.

### 7.4.4. Intergranular corrosion

Intergranular corrosion is the preferential corrosion of material at the grain (crystal) boundaries. Though the loss of material will be small, intergranular corrosion can cause the catastrophic failure of equipment. Intergranular corrosion is a common form of attack on alloys but occurs rarely with pure metals. The attack is usually caused by a differential couple being set up between impurities existing at the grain boundary. Impurities will tend to accumulate at the grain boundaries after heat treatment. The classic example of intergranular corrosion in chemical plant is the weld decay of unestablished stainless steel. This is caused by the precipitation of chromium carbides at the grain boundaries in a zone adjacent to the weld, where the temperature has been between 500–800°C during welding. Weld decay can be avoided by annealing after welding, if practical; or by using low carbon grades (<0.3 per cent C); or grades stabilised by the addition of titanium or niobium.

### 7.4.5. Effect of stress

Corrosion rate and the form of attack can be changed if the material is under stress. Generally, the rate of attack will not change significantly within normal design stress values. However, for some combinations of metal, corrosive media and temperature, the phenomenon called stress cracking can occur. This is the general name given to a form

of attack in which cracks are produced that grow rapidly, and can cause premature, brittle failure, of the metal. The conditions necessary for stress corrosion cracking to occur are:

1. Simultaneous stress and corrosion.
2. A specific corrosive substance; in particular the presence of  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ , or  $\text{NH}_4^+$  ions.

Mild stress can cause cracking; the residual stresses from fabrication and welding are sufficient.

For a general discussion of the mechanism of stress corrosion cracking see Fontana (1986).

Some classic examples of stress corrosion cracking are:

The season cracking of brass cartridge cases.

Caustic embrittlement of steel boilers.

The stress corrosion cracking of stainless steels in the presence of chloride ions.

Stress corrosion cracking can be avoided by selecting materials that are not susceptible in the specific corrosion environment; or, less certainly, by stress relieving by annealing after fabrication and welding.

Comprehensive tables of materials susceptible to stress corrosion cracking in specific chemicals are given by Moore (1979). Moore's tables are taken from the corrosion data survey published by NACE (1974).

The term corrosion fatigue is used to describe the premature failure of materials in corrosive environments caused by cyclic stresses. Even mildly corrosive conditions can markedly reduce the fatigue life of a component. Unlike stress corrosion cracking, corrosion fatigue can occur in any corrosive environment and does not depend on a specific combination of corrosive substance and metal. Materials with a high resistance to corrosion must be specified for critical components subjected to cyclic stresses.

#### **7.4.6. Erosion-corrosion**

The term erosion-corrosion is used to describe the increased rate of attack caused by a combination of erosion and corrosion. If a fluid stream contains suspended particles, or where there is high velocity or turbulence, erosion will tend to remove the products of corrosion and any protective film, and the rate of attack will be markedly increased. If erosion is likely to occur, more resistant materials must be specified, or the material surface protected in some way. For example, plastics inserts are used to prevent erosion-corrosion at the inlet to heat-exchanger tubes.

#### **7.4.7. High-temperature oxidation**

Corrosion is normally associated with aqueous solutions but oxidation can occur in dry conditions. Carbon and low alloy steels will oxidise rapidly at high temperatures and their use is limited to temperatures below 500°C.

Chromium is the most effective alloying element to give resistance to oxidation, forming a tenacious oxide film. Chromium alloys should be specified for equipment subject to temperatures above 500°C in oxidising atmospheres.

### 7.4.8. Hydrogen embrittlement

Hydrogen embrittlement is the name given to the loss of ductility caused by the absorption (and reaction) of hydrogen in a metal. It is of particular importance when specifying steels for use in hydrogen reforming plant. Alloy steels have a greater resistance to hydrogen embrittlement than the plain carbon steels. A chart showing the suitability of various alloy steels for use in hydrogen atmospheres, as a function of hydrogen partial pressure and temperature, is given in the NACE (1974) corrosion data survey. Below 500°C plain carbon steel can be used.

## 7.5. SELECTION FOR CORROSION RESISTANCE

In order to select the correct material of construction, the process environment to which the material will be exposed must be clearly defined. Additional to the main corrosive chemicals present, the following factors must be considered:

1. Temperature—affects corrosion rate and mechanical properties.
2. Pressure.
3. pH.
4. Presence of trace impurities—stress corrosion.
5. The amount of aeration—differential oxidation cells.
6. Stream velocity and agitation—erosion-corrosion.
7. Heat-transfer rates—differential temperatures.

The conditions that may arise during abnormal operation, such as at start-up and shutdown, must be considered, in addition to normal, steady state, operation.

### **Corrosion charts**

The resistance of some commonly used materials to a range of chemicals is shown in Appendix C. More comprehensive corrosion data, covering most of the materials used in the construction of process plant, in a wide range of corrosive media, are given by, Rabald (1968), NACE (1974), Hamner (1974), Perry *et al.* (1997) and Schweitzer (1976) (1989) (1998).

The twelve volume *Dechema Corrosion Handbook* is an extensive guide to the interaction of corrosive media with materials, Dechema (1987).

These corrosion guides can be used for the preliminary screening of materials that are likely to be suitable, but the fact that published data indicate that a material is suitable cannot be taken as a guarantee that it will be suitable for the process environment being considered. Slight changes in the process conditions, or the presence of unsuspected trace impurities, can markedly change the rate of attack or the nature of the corrosion. The guides will, however, show clearly those materials that are manifestly unsuitable. Judgement, based on experience with the materials in similar processes environments, must be used when assessing published corrosion data.

Pilot plant tests, and laboratory corrosion tests under simulated plant conditions, will help in the selection of suitable materials if actual plant experience is not available. Care is needed in the interpretation of laboratory tests.

The advice of the technical service department of the company supplying the materials should also be sought.

## 7.6. MATERIAL COSTS

An indication of the cost of some commonly used metals is given in Table 7.5. The actual cost of metals and alloys will fluctuate quite widely, depending on movements in the world metal exchanges.

Table 7.5. Basic cost of metals (mid-2004)

Metal	£/tonne	US\$/US ton
Carbon steel	300	500
Low alloy steel (Cr-Mo)	400–500	700–850
Austenitic stainless steel		
304	1400	2400
316	1900	3200
Copper	1500	2500
Aluminium	900	1500
Aluminium alloy	850	1400
Nickel	6400	11,000
Monel	5000	8500
Titanium	20,000	34,000

The quantity of a material used will depend on the material density and strength (design stress) and these must be taken into account when comparing material costs. Moore (1970) compares costs by calculating a cost rating factor defined by the equation:

$$\text{Cost rating} = \frac{C \times \rho}{\sigma_d} \quad (7.2)$$

where  $C$  = cost per unit mass, £/kg,

$\rho$  = density, kg/m<sup>3</sup>,

$\sigma_d$  = design stress, N/mm<sup>2</sup>.

His calculated cost ratings, relative to the rating for mild steel (low carbon), are shown in Table 7.6. Materials with a relatively high design stress, such as stainless and low alloy steels, can be used more efficiently than carbon steel.

The relative cost of equipment made from different materials will depend on the cost of fabrication, as well as the basic cost of the material. Unless a particular material requires special fabrication techniques, the relative cost of the finished equipment will be lower than the relative bare material cost. For example; the purchased cost of a stainless-steel storage tank will be 2 to 3 times the cost of the same tank in carbon steel, whereas the relative cost of the metals is between 5 to 8.

If the corrosion rate is uniform, then the optimum material can be selected by calculating the annual costs for the possible candidate materials. The annual cost will depend on the predicted life, calculated from the corrosion rate, and the purchased cost of the equipment. In a given situation, it may prove more economic to install a cheaper material with a high corrosion rate and replace it frequently; rather than select a more resistant but more expensive material. This strategy would only be considered for relatively simple

Table 7.6. Relative cost ratings for metals

		Design stress (N/mm <sup>2</sup> )
Carbon steel	1	100
Al-alloys (Mg)	4	70
Stainless steel 18/8 (Ti)	5	130
Inconel	12	140
Brass	10–15	76
Al-bronzes	16	87
Aluminium	18	14
Monel	19	120
Copper	27	46
Nickel	35	70

*Note:* the design stress figures are shown for the purposes of illustration only and should not be used as design values.

equipment with low fabrication costs, and where premature failure would not cause a serious hazard. For example, carbon steel could be specified for an aqueous effluent line in place of stainless steel, accepting the probable need for replacement. The pipe wall thickness would be monitored *in situ* frequently to determine when replacement was needed.

The more expensive, corrosion-resistant, alloys are frequently used as a cladding on carbon steel. If a thick plate is needed for structural strength, as for pressure vessels, the use of clad materials can substantially reduce the cost.

## 7.7. CONTAMINATION

With some processes, the prevention of the contamination of a process stream, or a product, by certain metals, or the products of corrosion, overrides any other considerations when selecting suitable materials. For instance, in textile processes, stainless steel or aluminium is often used in preference to carbon steel, which would be quite suitable except that any slight rusting will mark the textiles (iron staining).

With processes that use catalysts, care must be taken to select materials that will not cause contamination and poisoning of the catalyst.

Some other examples that illustrate the need to consider the effect of contamination by trace quantities of other materials are:

1. For equipment handling acetylene the pure metals, or alloys containing copper, silver, mercury, gold, must be avoided to prevent the formation of explosive acetylides.
2. The presence of trace quantities of mercury in a process stream can cause the catastrophic failure of brass heat-exchanger tubes, from the formation of a mercury-copper amalgam. Incidents have occurred where the contamination has come from unsuspected sources, such as the failure of mercury-in-steel thermometers.
3. In the Flixborough disaster (see Chapter 9), there was evidence that the stress corrosion cracking of a stainless-steel pipe had been caused by zinc contamination from galvanised-wire supporting lagging.

### 7.7.1. Surface finish

In industries such as the food, pharmaceutical, biochemical, and textile industries, the surface finish of the material is as important as the choice of material, to avoid contamination.

Stainless steel is widely used, and the surfaces, inside and out, are given a high finish by abrasive blasting and mechanical polishing. This is done for the purposes of hygiene; to prevent material adhering to the surface; and to aid cleaning and sterilisation. The surface finishes required in food processing are discussed by Timperley (1984) and Jowitt (1980).

A good surface finish is important in textile fibre processing to prevent the fibres snagging.

## 7.8. COMMONLY USED MATERIALS OF CONSTRUCTION

The general mechanical properties, corrosion resistance, and typical areas of use of some of the materials commonly used in the construction of chemical plant are given in this section. The values given are for a typical, representative, grade of the material or alloy. The multitude of alloys used in chemical plant construction is known by a variety of trade names, and code numbers designated in the various national standards. With the exception of the stainless steels, no attempt has been made in this book to classify the alloys discussed by using one or other of the national standards; the commonly used, generic, names for the alloys have been used. For the full details of the properties and compositions of the grades available in a particular class of alloy, and the designated code numbers, reference should be made to the appropriate national code, to the various handbooks, or to manufacturers' literature. For the United Kingdom standards, the British Standards Institute Catalogue should be consulted.

The US trade names and codes are given by Perry *et al.* (1997). A comprehensive review of the engineering materials used for chemical and process plant can be found in the book by Evans (1974).

### 7.8.1. Iron and steel

Low carbon steel (mild steel) is the most commonly used engineering material. It is cheap; is available in a wide range of standard forms and sizes; and can be easily worked and welded. It has good tensile strength and ductility.

The carbon steels and iron are not resistant to corrosion, except in certain specific environments, such as concentrated sulphuric acid and the caustic alkalis. They are suitable for use with most organic solvents, except chlorinated solvents; but traces of corrosion products may cause discoloration.

Mild steel is susceptible to stress-corrosion cracking in certain environments.

The corrosion resistance of the low alloy steels (less than 5 per cent of alloying elements), where the alloying elements are added to improve the mechanical strength and not for corrosion resistance, is not significantly different from that of the plain carbon steels.

A comprehensive reference covering the properties and application of steels, including the stainless steels, is the book by Llewellyn (1992). The use of carbon steel in the construction of chemical plant is discussed by Clark (1970).



The high silicon irons (14 to 15 per cent Si) have a high resistance to mineral acids, except hydrofluoric acid. They are particularly suitable for use with sulphuric acid at all concentrations and temperatures. They are, however, very brittle.

### 7.8.2. Stainless steel

The stainless steels are the most frequently used corrosion resistant materials in the chemical industry.

To impart corrosion resistance the chromium content must be above 12 per cent, and the higher the chromium content, the more resistant is the alloy to corrosion in oxidising conditions. Nickel is added to improve the corrosion resistance in non-oxidising environments.

#### *Types*

A wide range of stainless steels is available, with compositions tailored to give the properties required for specific applications. They can be divided into three broad classes according to their microstructure:

1. Ferritic: 13–20 per cent Cr, < 0.1 per cent C, with no nickel
2. Austenitic: 18–20 per cent Cr, > 7 per cent Ni
3. Martensitic: 12–10 per cent Cr, 0.2 to 0.4 per cent C, up to 2 per cent Ni

The uniform structure of Austenite (fcc, with the carbides in solution) is the structure desired for corrosion resistance, and it is these grades that are widely used in the chemical industry. The composition of the main grades of austenitic steels, and the US, and equivalent UK designations are shown in Table 7.7. Their properties are discussed below.

Type 304 (the so-called 18/8 stainless steels): the most generally used stainless steel. It contains the minimum Cr and Ni that give a stable austenitic structure. The carbon content is low enough for heat treatment not to be normally needed with thin sections to prevent weld decay (see Section 7.4.4).

Type 304L: low carbon version of type 304 (< 0.03 per cent C) used for thicker welded sections, where carbide precipitation would occur with type 304.

Type 321: a stabilised version of 304, stabilised with titanium to prevent carbide precipitation during welding. It has a slightly higher strength than 304L, and is more suitable for high-temperature use.

Type 347: stabilised with niobium.

Type 316: in this alloy, molybdenum is added to improve the corrosion resistance in reducing conditions, such as in dilute sulphuric acid, and, in particular, to solutions containing chlorides.

Type 316L: a low carbon version of type 316, which should be specified if welding or heat treatment is liable to cause carbide precipitation in type 316.

Types 309/310: alloys with a high chromium content, to give greater resistance to oxidation at high temperatures. Alloys with greater than 25 per cent Cr are susceptible to embrittlement due to sigma phase formation at temperatures above 500°C. Sigma phase is an intermetallic compound, FeCr. The formation of the sigma phase in austenitic stainless steels is discussed by Hills and Harries (1960).

Table 7.7. Commonly used grades of austenitic stainless steel

Specification no.		Composition per cent							
BS 1501	AISI	C max	Si max	Mn max	Cr range	Ni range	Mo range	Ti	Nb
801B	304	0.08	—	2.00	17.5 20.0	8.0 11.0	—	—	—
810 C	304 ELC	0.03	1.00	2.00	17.5 20.0	10 min	—	—	—
801 Ti	321	0.12	1.00	2.00	17.0 20.0	7.5 min	—	4 × C	—
801 Nb	347	0.08	1.00	2.00	17.0 20.0	9 min	—	—	10 × C
821 Ti	—	0.12	1.00	2.00	17.0 20.0	25 min	—	4 × C	—
845 B	316	0.08	1.00	2.00	16.5 18.5	10 min	2.25 3.00	—	—
845 Ti	—	0.08	0.06	2.00	16.5 18.5	10 min	2.25 3.00	4 × C	—
846	—	0.08	1.00	2.00	18.0 20.0	11.0 14.0	3.0 4.0	—	—

S and P 0.045 per cent all grades.

AISI American Iron and Steel Institute.

Table 7.8. Comparative strength of stainless steel

Temperature °C		300	400	500	600
Typical design stress N/mm <sup>2</sup>	mild steel	77	62	31	—
	stainless 18/8	108	100	92	62

### **Mechanical properties**

The austenitic stainless steels have greater strength than the plain carbon steels, particularly at elevated temperatures (see Table 7.8).

As was mentioned in Section 7.3.7, the austenitic stainless steels, unlike the plain carbon steels, do not become brittle at low temperatures. It should be noted that the thermal conductivity of stainless steel is significantly lower than that of mild steel.

Typical at 100°C values are, type 304 (18/8) 16 W/m°C

mild steel 60 W/m°C

Austenitic stainless steels are non-magnetic in the annealed condition.

### **General corrosion resistance**

The higher the alloying content, the better the corrosion resistance over a wide range of conditions, strongly oxidising to reducing, but the higher the cost. A ranking in order of

increasing corrosion resistance, taking type 304 as 1, is given below:

304	304L	321	316	316L	310
1.0	1.1	1.1	1.25	1.3	1.6

Intergranular corrosion (weld decay) and stress corrosion cracking are problems associated with the use of stainless steels, and must be considered when selecting types suitable for use in a particular environment. Stress corrosion cracking in stainless steels can be caused by a few ppm of chloride ions (see Section 7.4.5).

In general, stainless steels are used for corrosion resistance when oxidising conditions exist. Special types, or other high nickel alloys, should be specified if reducing conditions are likely to occur. The properties, corrosion resistance, and uses of the various grades of stainless steel are discussed fully by Peckner and Bernstein (1977). A comprehensive discussion of the corrosion resistance of stainless steels is given in Sedriks (1979).

Stress corrosion cracking in stainless steels is discussed by Turner (1989).

### ***High alloy content stainless steels***

Super austenitic, high nickel, stainless steels, containing between 29 to 30 per cent nickel and 20 per cent chromium, have a good resistance to acids and acid chlorides. They are more expensive than the lower alloy content, 300 series, of austenitic stainless steels.

Duplex, and super-duplex stainless steels, contain high percentages of chromium. They are called duplex because their structure is a mixture of the austenitic and ferritic phases. They have a better corrosion resistance than the austenitic stainless steels and are less susceptible to stress corrosion cracking. The chromium content of duplex stainless steels is around 20 per cent, and around 25 per cent in the super-duplex grades. The super-duplex steels were developed for use in aggressive off-shore environments.

The duplex range of stainless steels can be readily cast, wrought and machined. Problems can occur in welding, due to the need to keep the correct balance of ferrite and austenite in the weld area, but this can be overcome using the correct welding materials and procedures.

The cost of the duplex grades is comparable with the 316 steels. Super-duplex is around fifty per cent higher than the cost of duplex.

The selection and properties of duplex stainless steels are discussed by Bendall and Guha (1990), and Warde (1991).

### **7.8.3. Nickel**

Nickel has good mechanical properties and is easily worked. The pure metal (>99 per cent) is not generally used for chemical plant, its alloys being preferred for most applications. The main use is for equipment handling caustic alkalis at temperatures above that at which carbon steel could be used; above 70°C. Nickel is not subject to corrosion cracking like stainless steel.

#### **7.8.4. Monel**

Monel, the classic nickel-copper alloy with the metals in the ratio 2 : 1, is probably, after the stainless steels, the most commonly used alloy for chemical plant. It is easily worked and has good mechanical properties up to 500°C. It is more expensive than stainless steel but is not susceptible to stress-corrosion cracking in chloride solutions. Monel has good resistance to dilute mineral acids and can be used in reducing conditions, where the stainless steels would be unsuitable. It may be used for equipment handling, alkalies, organic acids and salts, and sea water.

#### **7.8.5. Inconel**

Inconel (typically 76 per cent Ni, 7 per cent Fe, 15 per cent Cr) is used primarily for acid resistance at high temperatures. It maintains its strength at elevated temperature and is resistant to furnace gases, if sulphur free.

#### **7.8.6. The Hastelloys**

The trade name Hastelloy covers a range of nickel, chromium, molybdenum, iron alloys that were developed for corrosion resistance to strong mineral acids, particularly HCl. The corrosion resistance, and use, of the two main grades, Hastelloy B (65 per cent Ni, 28 per cent Mo, 6 per cent Fe) and Hastelloy C (54 per cent Ni, 17 per cent Mo, 15 per cent Cr, 5 per cent Fe), are discussed in papers by Weisert (1952a,b).

#### **7.8.7. Copper and copper alloys**

Pure copper is not widely used for chemical equipment. It has been used traditionally in the food industry, particularly in brewing. Copper is a relatively soft, very easily worked metal, and is used extensively for small-bore pipes and tubes.

The main alloys of copper are the brasses, alloyed with zinc, and the bronzes, alloyed with tin. Other, so-called bronzes are the aluminium bronzes and the silicon bronzes.

Copper is attacked by mineral acids, except cold, dilute, unaerated sulphuric acid. It is resistant to caustic alkalies, except ammonia, and to many organic acids and salts. The brasses and bronzes have a similar corrosion resistance to the pure metal. Their main use in the chemical industry is for valves and other small fittings, and for heat-exchanger tubes and tube sheets. If brass is used, a grade must be selected that is resistant to dezincification.

The cupro-nickel alloys (70 per cent Cu) have a good resistance to corrosion-erosion and are used for heat-exchanger tubes, particularly where sea water is used as a coolant.

#### **7.8.8. Aluminium and its alloys**

Pure aluminium lacks mechanical strength but has higher resistance to corrosion than its alloys. The main structural alloys used are the Duralumin (Dural) range of aluminium-copper

alloys (typical composition 4 per cent Cu, with 0.5 per cent Mg) which have a tensile strength equivalent to that of mild steel. The pure metal can be used as a cladding on Dural plates, to combine the corrosion resistance of the pure metal with the strength of the alloy. The corrosion resistance of aluminium is due to the formation of a thin oxide film (as with the stainless steels). It is therefore most suitable for use in strong oxidising conditions. It is attacked by mineral acids, and by alkalies; but is suitable for concentrated nitric acid, greater than 80 per cent. It is widely used in the textile and food industries, where the use of mild steel would cause contamination. It is also used for the storage and distribution of demineralised water.

### **7.8.9. Lead**

Lead was one of the traditional materials of construction for chemical plant but has now, due to its price, been largely replaced by other materials, particularly plastics. It is a soft, ductile material, and is mainly used in the form of sheets (as linings) or pipe. It has a good resistance to acids, particularly sulphuric.

### **7.8.10. Titanium**

Titanium is now used quite widely in the chemical industry, mainly for its resistance to chloride solutions, including sea water and wet chlorine. It is rapidly attacked by dry chlorine, but the presence of as low a concentration of moisture as 0.01 per cent will prevent attack. Like the stainless steels, titanium depends for its resistance on the formation of an oxide film.

Alloying with palladium (0.15 per cent) significantly improves the corrosion resistance, particularly to HCl. Titanium is being increasingly used for heat exchangers, for both shell and tube, and plate exchangers; replacing cupro-nickel for use with sea water.

The use of titanium for corrosion resistance is discussed by Deily (1997).

### **7.8.11. Tantalum**

The corrosion resistance of tantalum is similar to that of glass, and it has been called a metallic glass. It is expensive, about five times that of stainless steel, and is used for special applications, where glass or a glass lining would not be suitable. Tantalum plugs are used to repair glass-lined equipment.

The use of tantalum as a material of construction in the chemical industry is discussed by Fensom and Clark (1984) and Rowe (1994) (1999).

### **7.8.12. Zirconium**

Zirconium and zirconium alloys are used in the nuclear industry, because of their low neutron absorption cross-section and resistance to hot water at high pressures.

In the chemical industry zirconium is finding use where resistance to hot and boiling acids is required: nitric, sulphuric, and particularly hydrochloric. Its resistance is equivalent to that of tantalum but zirconium is less expensive, similar in price to high nickel steel. Rowe (1999) gives a brief review of the properties and use of zirconium for chemical plant.

### 7.8.13. Silver

Silver linings are used for vessels and equipment handling hydrofluoric acid. It is also used for special applications in the food and pharmaceutical industries where it is vital to avoid contamination of the product.

### 7.8.14. Gold

Because of its high cost gold is rarely used as a material of construction. It is highly resistant to attack by dilute nitric acid and hot concentrated sulphuric acid, but is dissolved by aqua regia (a mixture of concentrated nitric and sulphuric acids). It is attacked by chlorine and bromine, and forms an amalgam with mercury.

It has been used as thin plating on condenser tubes and other surfaces.

### 7.8.15. Platinum

Platinum has a high resistance to oxidation at high temperature. One of its main uses has been, in the form of an alloy with copper, in the manufacture of the spinnerets used in synthetic textile spinning processes.

## 7.9. PLASTICS AS MATERIALS OF CONSTRUCTION FOR CHEMICAL PLANT

Plastics are being increasingly used as corrosion-resistant materials for chemical plant construction. They can be divided into two broad classes:

1. Thermoplastic materials, which soften with increasing temperature; for example, polyvinyl chloride (PVC) and polyethylene.
2. Thermosetting materials, which have a rigid, cross-linked structure; for example, the polyester and epoxy resins.

Details of the chemical composition and properties of the wide range of plastics used as engineering material can be found in the books by Butt and Wright (1980) and Evans (1974).

The biggest use of plastics is for piping; sheets are also used for lining vessels and for fabricated ducting and fan casings. Mouldings are used for small items; such as, pump impellers, valve parts and pipe fittings.

The mechanical strength and operating temperature of plastics are low compared with that of metals. The mechanical strength, and other properties, can be modified by the addition of fillers and plasticisers. When reinforced with glass or carbon fibres thermosetting plastics can have a strength equivalent to mild steel, and are used for pressure vessels and pressure piping. Unlike metals, plastics are flammable. Plastics can be considered to complement metals as corrosion-resistant materials of construction. They generally have good resistance to dilute acids and inorganic salts, but suffer degradation in organic solvents that would not attack metals. Unlike metals, plastics can absorb solvents, causing swelling and softening. The properties and typical areas of use of the main plastics used for chemical plant are reviewed briefly in the following sections. A comprehensive discussion of the use of plastics as corrosion-resistant materials is given in a book by Fontana (1986). The mechanical properties and relative cost of plastics are given in Table 7.9.

Table 7.9. Mechanical properties and relative cost of polymers

Material	Tensile strength (N/mm <sup>2</sup> )	Elastic modulus (kN/mm <sup>2</sup> )	Density (kg/m <sup>3</sup> )	Relative cost
PVC	55	3.5	1400	1.5
Polyethylene (low density)	12	0.2	900	1.0
Polypropylene	35	1.5	900	1.5
PTFE	21	1.0	2100	30.0
GRP polyester	100	7.0	1500	3.0
GRP epoxy	250	14.0	1800	5.0

Approximate cost relative to polyethylene, volumetric basis.

### 7.9.1. Poly-vinyl chloride (PVC)

PVC is probably the most commonly used thermoplastic material in the chemical industry. Of the available grades, rigid (unplasticised) PVC is the most widely used. It is resistant to most inorganic acids, except strong sulphuric and nitric, and inorganic salt solutions. It is unsuitable, due to swelling, for use with most organic solvents. The maximum operating temperature for PVC is low, 60°C. The use of PVC as a material of construction in chemical engineering is discussed in a series of articles by Mottram and Lever (1957).

### 7.9.2. Polyolefines

Low-density polyethylene (polythene) is a relatively cheap, tough, flexible plastic. It has a low softening point and is not suitable for use above about 60°C. The higher density polymer (950 kg/m<sup>3</sup>) is stiffer, and can be used at higher temperatures. Polypropylene is a stronger material than the polyethylenes and can be used at temperatures up to 120°C.

The chemical resistance of the polyolefines is similar to that of PVC.

### 7.9.3. Polytetrafluoroethylene (PTFE)

PTFE, known under the trade names Teflon and Fluon, is resistant to all chemicals, except molten alkalis and fluorine, and can be used at temperatures up to 250°C. It is a relatively weak material, but its mechanical strength can be improved by the addition of fillers (glass and carbon fibres). It is expensive and difficult to fabricate. PTFE is used extensively for gaskets and gland packings. As a coating, it is used to confer non-stick properties to surfaces, such as filter plates. It can also be used as a liner for vessels.

### 7.9.4. Polyvinylidene fluoride (PVDF)

PVDF has properties similar to PTFE but is easier to fabricate. It has good resistance to inorganic acids and alkalis, and organic solvents. It is limited to a maximum operating temperature of 140°C.

### 7.9.5. Glass-fibre reinforced plastics (GRP)

The polyester resins, reinforced with glass fibre, are the most common thermosetting plastics used for chemical plant. Complex shapes can be easily formed using the techniques developed for working with reinforced plastics. Glass-reinforced plastics are relatively

strong and have a good resistance to a wide range of chemicals. The mechanical strength depends on the resin used; the form of the reinforcement (chopped mat or cloth); and the ratio of resin to glass.

By using special techniques, in which the reinforcing glass fibres are wound on in the form of a continuous filament, high strength can be obtained, and this method is used to produce pressure vessels.

The polyester resins are resistant to dilute mineral acids, inorganic salts and many solvents. They are less resistant to alkalis.

Glass-fibre-reinforced epoxy resins are also used for chemical plant but are more expensive than the polyester resins. In general they are resistant to the same range of chemicals as the polyesters, but are more resistant to alkalis.

The chemical resistance of GRP is dependent on the amount of glass reinforcement used. High ratios of glass to resin give higher mechanical strength but generally lower resistance to some chemicals. The design of chemical plant equipment in GRP is the subject of a book by Malleison (1969); see also Shaddock (1971) and Baines (1984).

### **7.9.6. Rubber**

Rubber, particularly in the form of linings for tanks and pipes, has been extensively used in the chemical industry for many years. Natural rubber is most commonly used, because of its good resistance to acids (except concentrated nitric) and alkalis. It is unsuitable for use with most organic solvents.

Synthetic rubbers are also used for particular applications. Hypalon (trademark, E. I. du Pont de Nemours) has a good resistance to strongly oxidising chemicals and can be used with nitric acid. It is unsuitable for use with chlorinated solvents. Viton (trademark, E. I. du Pont de Nemours) has a better resistance to solvents, including chlorinated solvents, than other rubbers. Both Hypalon and Viton are expensive, compared with other synthetic, and natural, rubbers.

The use of natural rubber lining is discussed by Saxman (1965), and the chemical resistance of synthetic rubbers by Evans (1963).

Butt and Wright (1984) give an authoritative account of the application and uses of rubber and plastics linings and coatings.

## **7.10. CERAMIC MATERIALS (SILICATE MATERIALS)**

Ceramics are compounds of non-metallic elements and include the following materials used for chemical plant:

Glass, the borosilicate glasses (hard glass).

Stoneware.

Acid-resistant bricks and tiles.

Refractory materials.

Cements and concrete.

Ceramic materials have a cross-linked structure and are therefore brittle.



### 7.10.1. Glass

Borosilicate glass (known by several trade names, including Pyrex) is used for chemical plant as it is stronger than the soda glass used for general purposes; it is more resistant to thermal shock and chemical attack.

Glass equipment is available from several specialist manufacturers. Pipes and fittings are produced in a range of sizes, up to 0.5 m. Special equipment, such as heat exchangers, is available and, together with the larger sizes of pipe, is used to construct distillation and absorption columns. Teflon gaskets are normally used for jointing glass equipment and pipe.

Where failure of the glass could cause injury, pipes and equipment should be protected by external shielding or wrapping with plastic tape.

Glass linings, also known as glass enamel, have been used on steel and iron vessels for many years. Borosilicate glass is used, and the thickness of the lining is about 1 mm. The techniques used for glass lining, and the precautions to be taken in the design and fabrication of vessels to ensure a satisfactory lining, are discussed by Landels and Stout (1970). Borosilicate glass is resistant to acids, salts and organic chemicals. It is attacked by the caustic alkalis and fluorine.

### 7.10.2. Stoneware

Chemical stoneware is similar to the domestic variety, but of higher quality; stronger and with a better glaze. It is available in a variety of shapes for pipe runs and columns. As for glass, it is resistant to most chemicals, except alkalis and fluorine. The composition and properties of chemical stoneware are discussed by Holdridge (1961). Stoneware and porcelain shapes are used for packing absorption and distillation columns (see Chapter 11).

### 7.10.3. Acid-resistant bricks and tiles

High-quality bricks and tiles are used for lining vessels, ditches and to cover floors. The linings are usually backed with a corrosion-resistant membrane of rubber or plastic, placed behind the tiles, and special acid-resistant cements are used for the joints. Brick and tile linings are covered in a book by Falcke and Lorentz (1985).

### 7.10.4. Refractory materials (refractories)

Refractory bricks and cements are needed for equipment operating at high temperatures; such as, fired heaters, high-temperature reactors and boilers.

The refractory bricks in common use are composed of mixtures of silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ). The quality of the bricks is largely determined by the relative amounts of these materials and the firing temperature. Mixtures of silica and alumina form a eutectic (94.5 per cent  $\text{SiO}_2$ ,  $1545^\circ\text{C}$ ) and for a high refractoriness under load (the ability to resist distortion at high temperature) the composition must be well removed from the eutectic composition. The highest quality refractory bricks, for use in load-bearing structures at high temperatures, contain high proportions of silica or alumina. "Silica bricks", containing greater than 98 per cent  $\text{SiO}_2$ , are used for general furnace construction. High alumina bricks, 60 per cent  $\text{Al}_2\text{O}_3$ , are used for special furnaces where resistance to attack by alkalis is important; such as lime and cement kilns. Fire bricks, typical

composition 50 per cent  $\text{SiO}_2$ , 40 per cent  $\text{Al}_2\text{O}_3$ , balance  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ , are used for general furnace construction. Silica can exist in a variety of allotropic forms, and bricks containing a high proportion of silica undergo reversible expansion when heated up to working temperature. The higher the silica content the greater the expansion, and this must be allowed for in furnace design and operation.

Ordinary fire bricks, fire bricks with a high porosity, and special bricks composed of diatomaceous earths are used for insulating walls.

Full details of the refractory materials used for process and metallurgical furnaces can be found in the books by Norton (1968) and Lyle (1947).

### 7.11. CARBON

Impervious carbon, impregnated with chemically resistant resins, is used for specialised equipment; particularly heat exchangers. It has a high conductivity and a good resistance to most chemicals, except oxidising acids, of concentrations greater than 30 per cent. Carbon tubes can be used in conventional shell and tube exchanger arrangements; or proprietary designs can be used, in which the fluid channels are formed in blocks of carbon; see Hilland (1960) and Denyer (1991).

### 7.12. PROTECTIVE COATINGS

A wide range of paints and other organic coatings is used for the protection of mild steel structures. Paints are used mainly for protection from atmospheric corrosion. Special chemically resistant paints have been developed for use on chemical process equipment. Chlorinated rubber paints and epoxy-based paints are used. In the application of paints and other coatings, good surface preparation is essential to ensure good adhesion of the paint film or coating.

Brief reviews of the paints used to protect chemical plant are given by Ruff (1984) and Hullcoop (1984).

### 7.13. DESIGN FOR CORROSION RESISTANCE

The life of equipment subjected to corrosive environments can be increased by proper attention to design details. Equipment should be designed to drain freely and completely. The internal surfaces should be smooth and free from crevasses where corrosion products and other solids can accumulate. Butt joints should be used in preference to lap joints. The use of dissimilar metals in contact should be avoided, or care taken to ensure that they are effectively insulated to avoid galvanic corrosion. Fluid velocities and turbulence should be high enough to avoid the deposition of solids, but not so high as to cause erosion-corrosion.

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## 7.15. NOMENCLATURE

	Dimensions in <b>MLT£</b>
<i>A</i> Area	<b>L<sup>2</sup></b>
<i>C</i> Cost of material	<b>£/M</b>
<i>t</i> Time	<b>T</b>
<i>w</i> Mass loss	<b>M</b>
$\rho$ Density	<b>ML<sup>-3</sup></b>
$\sigma_d$ Design stress	<b>ML<sup>-1</sup> T<sup>-2</sup></b>

## 7.16. PROBLEMS

- 7.1.** A pipeline constructed of carbon steel failed after 3 years operation. On examination it was found that the wall thickness had been reduced by corrosion to about half the original value. The pipeline was constructed of nominal 100 mm (4 in) schedule 40, pipe, inside diameter 102.3 mm (4.026 in), outside diameter 114.3 mm (4.5 in). Estimate the rate of corrosion in ipy and mm per year.
- 7.2.** The pipeline described in question 7.1 was used to carry wastewater to a hold-up tank. The effluent is not hazardous. A decision has to be made on what material to use to replace the pipe. Three suggestions have been made:
1. Replace with the same schedule carbon steel pipe and accept renewal at 3-year intervals.
  2. Replace with a thicker pipe, schedule 80, outside diameter 114.3 mm (4.5 in), inside diameter 97.2 mm (3.826 in).
  3. Use stainless steel pipe, which will not corrode.

The estimated cost of the pipes, per unit length is: schedule 40 carbon steel £3 (\$5), schedule 80 carbon steel £5 (\$8.3), stainless steel (304) schedule 40 £15 (\$24.8). Installation and fittings for all the materials adds £10 (\$16.5) per unit length.

The downtime required to replace the pipe does not result in a loss of production. If the expected future life of the plant is 7 years, recommend which pipe to use.

**7.3.** Choose a suitable material of construction for the following duties:

1. 98 per cent w/w sulphuric acid at 70 °C.
2. 5 per cent w/w sulphuric acid at 30 °C.
3. 30 per cent w/w hydrochloric acid at 50 °C.
4. 5 per cent aqueous sodium hydroxide solution at 30 °C.
5. Concentrated aqueous sodium hydroxide solution at 50 °C.
6. 5 per cent w/w nitric acid at 30 °C.
7. Boiling concentrated nitric acid.
8. 10 per cent w/w sodium chloride solution.
9. A 5 per cent w/w solution of cuprous chloride in hydrochloric acid.
10. 10 per cent w/w hydrofluoric acid.

In each case, select the material for a 50 mm pipe operating at approximately 2 bar pressure.

**7.4.** Suggest suitable materials of construction for the following applications:

1. A 10,000 m<sup>3</sup> storage tank for toluene.
2. A 5.0 m<sup>3</sup> tank for storing a 30% w/w aqueous solution of sodium chloride.
3. A 2m diameter, 20 m high distillation column, distilling acrylonitrile.
4. A 100 m<sup>3</sup> storage tank for strong nitric acid.
5. A 500 m<sup>3</sup> aqueous waste hold-up tank. The wastewater pH can vary from 1 to 12. The wastewater will also contain traces of organic material.
6. A packed absorption column 0.5 m diameter, 3 m high, absorbing gaseous hydrochloric acid into water. The column will operate at essentially atmospheric pressure.

**7.5.** Aniline is manufactured by the hydrogenation of nitrobenzene in a fluidised bed reactor. The reactor operates at 250 °C and 20 bar. The reactor vessel is approximately 3 m diameter and 9 m high. Suggest suitable materials of construction for this reactor.

**7.6.** Methyl ethyl ketone (MEK) is manufactured by the dehydrogenation of 2-butanol using a shell and tube type reactor. Flue gases are used for heating and pass through the tubes. The flue gases will contain traces of sulphur dioxide. The reaction products include hydrogen.

The reaction takes place in the shell at a pressure of 3 bar and temperature of 500 °C. Select suitable materials for the tubes and shell.

**7.7.** In the manufacture of aniline by the hydrogenation of nitrobenzene, the off-gases from the reactor are cooled and the products and unreacted nitrobenzene condensed in a shell and tube exchanger. A typical composition of the condensate is, kmol/h: aniline 950, cyclo-hexylamine 10, water 1920, nitrobenzene 40. The gases enter the condenser at 230 °C and leave at 50 °C. The cooling water enters the tubes at 20 °C and leaves at 50 °C. Suggest suitable materials of construction for the shell and the tubes.

**7.8.** A slurry of acrylic polymer particles in water is held in storage tanks prior to filtering and drying. Plain carbon steel would be a suitable material for the tanks, but it is essential that the polymer does not become contaminated with iron in storage. Suggest some alternative materials of construction for the tanks.

## CHAPTER 8

# *Design Information and Data*

### 8.1. INTRODUCTION

Information on manufacturing processes, equipment parameters, materials of construction, costs and the physical properties of process materials are needed at all stages of design; from the initial screening of possible processes, to the plant start-up and production.

Sources of data on costs were discussed in Chapter 6 and materials of construction in Chapter 7. This chapter covers sources of information on manufacturing processes and physical properties; and the estimation of physical property data. Information on the types of equipment (unit operations) used in chemical process plants is given in Volume 2, and in the Chapters concerned with equipment selection and design in this Volume, Chapters 10, 11 and 12.

When a project is largely a repeat of a previous project, the data and information required for the design will be available in the Company's process files, if proper detailed records are kept. For a new project or process, the design data will have to be obtained from the literature, or by experiment (research laboratory and pilot plant), or purchased from other companies. The information on manufacturing processes available in the general literature can be of use in the initial stages of process design, for screening potential process; but is usually mainly descriptive, and too superficial to be of much use for detailed design and evaluation.

The literature on the physical properties of elements and compounds is extensive, and reliable values for common materials can usually be found. The principal sources of physical property data are listed in the references at the end of this chapter.

Where values cannot be found, the data required will have to be measured experimentally or estimated. Methods of estimating (predicting) the more important physical properties required for design are given in this chapter. A physical property data bank is given in Appendix C.

Readers who are unfamiliar with the sources of information, and the techniques used for searching the literature, should consult one of the many guides to the technical literature that have been published; such as those by Lord (2000) and Maizell (1998).

### 8.2. SOURCES OF INFORMATION ON MANUFACTURING PROCESSES

In this section the sources of information available in the open literature on commercial processes for the production of chemicals and related products are reviewed.

The chemical process industries are competitive, and the information that is published on commercial processes is restricted. The articles on particular processes published in the technical literature and in textbooks invariably give only a superficial account of the chemistry and unit operations used. They lack the detailed information needed on reaction kinetics, process conditions, equipment parameters, and physical properties needed for process design. The information that can be found in the general literature is, however, useful in the early stages of a project, when searching for possible process routes. It is often sufficient for a flow-sheet of the process to be drawn up and a rough estimate of the capital and production costs made.

The most comprehensive collection of information on manufacturing processes is probably the *Encyclopedia of Chemical Technology* edited by Kirk and Othmer (2001) (2003), which covers the whole range of chemical and associated products. Another encyclopedia covering manufacturing processes is that edited by McKetta (2001). Several books have also been published which give brief summaries of the production processes used for the commercial chemicals and chemical products. The most well known of these is probably Shreve's book on the chemical process industries, now updated by Austin and Basta (1998). Comyns (1993) lists named chemical manufacturing processes, with references.

The extensive German reference work on industrial processes, *Ullman's Encyclopedia of Industrial Technology*, is now available in an English translation, Ullman (2002).

Specialised texts have been published on some of the more important bulk industrial chemicals, such as that by Miller (1969) on ethylene and its derivatives; these are too numerous to list but should be available in the larger reference libraries and can be found by reference to the library catalogue.

Books quickly become outdated, and many of the processes described are obsolete, or at best obsolescent. More up-to-date descriptions of the processes in current use can be found in the technical journals. The journal *Hydrocarbon Processing* publishes an annual review of petrochemical processes, which was entitled *Petrochemical Developments* and is now called *Petrochemicals Notebook*; this gives flow-diagrams and brief process descriptions of new process developments. Patents are a useful source of information; but it should be remembered that the patentee will try to write the patent in a way that protects his invention, whilst disclosing the least amount of useful information to his competitors. The examples given in a patent to support the claims often give an indication of the process conditions used; though they are frequently examples of laboratory preparations, rather than of the full-scale manufacturing processes. Several guides have been written to help engineers understand the use of patents for the protection of inventions, and as sources of information; such as those by Auger (1992) and Gordon and Cookfair (2000).

### **World Wide Web**

It is worthwhile searching the Internet for information on processes, equipment, products and physical properties. Many manufacturers and government departments maintain web sites. In particular, up-to-date information can be obtained on the health and environmental effects of products.

### **Internet sources**

Many of the university libraries in the UK and USA provide information guides for the students and these are available on the Internet. A search using the key words such as “chemical engineering information” will usually find them. Some examples are:

Heriot-Watt University, Edinburgh, UK: [www.hw.ac.uk/lib](http://www.hw.ac.uk/lib)

Edinburgh, UK: [www.eevl.ac.uk](http://www.eevl.ac.uk)

University of Florida, USA: [www.che.ufl.edu/](http://www.che.ufl.edu/)

Karlsruhe, USA: [www.ciw.uni-karlsruhe.de/chem-eng](http://www.ciw.uni-karlsruhe.de/chem-eng)

### **Useful gateways**

EEVL (Edinburgh Engineering Virtual Library) Internet Guide to Engineering, Mathematics and Computing, [www.eevl.ac.uk](http://www.eevl.ac.uk)  
Heriot-Watt University, Edinburgh, UK

World-Wide Web Virtual Library: [www.che.ufl.edu/WWW-CHEindex.html](http://www.che.ufl.edu/WWW-CHEindex.html)  
University of Florida, USA

International Directory of Chemical Engineering URLs: [www.ciw.uni-karlsruhe.de/chem-eng.html](http://www.ciw.uni-karlsruhe.de/chem-eng.html)  
Karlsburg University, Germany

Many of the important sources of engineering information are subscription services. In the United Kingdom some of them can be accessed using the Athens service available to universities.

Another important source is the Knovel organisation. This provides online access to most standard reference books. It is a subscription service but can be accessed through many libraries, including those of the professional engineering institutions and some universities.

## **8.3. GENERAL SOURCES OF PHYSICAL PROPERTIES**

In this section those references that contain comprehensive compilations of physical property data are reviewed. Sources of data on specific physical properties are given in the remaining sections of the chapter.

*International Critical Tables* (1933) is still probably the most comprehensive compilation of physical properties, and is available in most reference libraries. Though it was first published in 1933, physical properties do not change, except in as much as experimental techniques improve, and ICT is still a useful source of engineering data. ICT is now available as an ebook and can be referenced on the Internet through Knovel (2003).

Tables and graphs of physical properties are given in many handbooks and textbooks on Chemical Engineering and related subjects. Many of the data given are duplicated from book to book, but the various handbooks do provide quick, easy access to data on the more commonly used substances.

An extensive compilation of thermophysical data has been published by Plenum Press, Touloukian (1970–77). This multiple-volume work covers conductivity, specific heat,



thermal expansion, viscosity and radiative properties (emittance, reflectance, absorptance and transmittance).

Elsevier have published a series of volumes on physical property and thermodynamic data. Those of use in design are included in the Bibliography at the end of this chapter.

The Engineering Sciences Data Unit (ESDU, [www.ihesedu.com](http://www.ihesedu.com)) was set up to provide validated data for engineering design, developed under the guidance and approval of engineers from industry, the universities and research laboratories. ESDU data include equipment design data and software and extensive high-quality physical property data—mostly for pure fluids that are in use in the oil and process industries and in university chemical and mechanical engineering departments worldwide.

Caution should be exercised when taking data from the literature, as typographical errors often occur. If a value looks doubtful it should be cross-checked in an independent reference, or by estimation.

The values of some properties will be dependent on the method of measurement; for example, surface tension and flash point, and the method used should be checked, by reference to the original paper if necessary, if an accurate value is required.

The results of research work on physical properties are reported in the general engineering and scientific literature. The *Journal of Chemical Engineering Data* specialises in publishing physical property data for use in chemical engineering design. A quick search of the literature for data can be made by using the abstracting journals; such as *Chemical Abstracts* (American Chemical Society) and *Engineering Index* (Engineering Index Inc., New York). *Engineering Index* is now called Engineering Information (Ei) and is a web-based reference source owned by Elsevier information ([www.ei.org](http://www.ei.org)).

Computerised physical property data banks have been set up by various organisations to provide a service to the design engineer. They can be incorporated into computer-aided design programs and are increasingly being used to provide reliable, authenticated, design data. Examples of such programs are the PPDS and the DIPPR™ databases.

PPDS (Physical Property Data Service) was originally developed in the United Kingdom by the Institution of Chemical Engineers and the National Physical Laboratory. It is now available as a Microsoft™ Windows version from NEL, a division of the TUV Sudeutschland Group ([www.nel.uk](http://www.nel.uk)). PPDS is made available to universities at a discount.

The DIPPR™ databases were developed in the United States by the Design Institute for Physical Properties of the American Institute of Chemical Engineers. The DIPPR™ projects are aimed at providing evaluated process design data for the design of chemical processes and equipment ([www.aiche.org/dippr/projects.htm](http://www.aiche.org/dippr/projects.htm)). The Project 801 has been made available to university departments; see Rowley *et al.* (2004) and <http://dippr.byu.edu/description/htm>.

## 8.4. ACCURACY REQUIRED OF ENGINEERING DATA

The accuracy needed depends on the use to which the data will be put. Before spending time and money searching for the most accurate value, or arranging for special measurements to be made, the designer must decide what accuracy is required; this will depend on several factors:

1. The level of design; less accuracy is obviously needed for rough scouting calculations, made to sort out possible alternative designs, than in the final stages of design; when money will be committed to purchase equipment, and for construction.
2. The reliability of the design methods; if there is some uncertainty in the techniques to be used, it is clearly a waste of time to search out highly accurate physical property data that will add little or nothing to the reliability of the final design.
3. The sensitivity to the particular property: how much will a small error in the property affect the design calculation. For example, it was shown in Chapter 4 that the estimation of the optimum pipe diameter is insensitive to viscosity. The sensitivity of a design method to errors in physical properties, and other data, can be checked by repeating the calculation using slightly altered values.

It is often sufficient to estimate a value for a property (sometimes even to make an intelligent guess) if the value has little effect on the final outcome of the design calculation. For example, in calculating the heat load for a reboiler or vaporiser an accurate value of the liquid specific heat is seldom needed, as the latent heat load is usually many times the sensible heat load and a small error in the sensible heat calculation will have little effect on the design. The designer must, however, exercise caution when deciding to use less reliable data, and to be sure that they are sufficiently accurate for his purpose. For example, it would be correct to use an approximate value for density when calculating the pressure drop in a pipe system where a small error could be tolerated, considering the other probable uncertainties in the design; but it would be quite unacceptable in the design of a decanter, where the operation depends on small differences in density.

Consider the accuracy of the equilibrium data required to calculate the number of equilibrium stages needed for the separation of a mixture of acetone and water by distillation (see Chapter 11, Example 11.2). Several investigators have published vapour-liquid equilibrium data for this system: Othmer *et al.* (1952), York and Holmes (1942), Kojima *et al.* (1968), Reinders and De Minjer (1947).

If the purity of the acetone product required is less than 95 per cent, inaccuracies in the  $v-l-e$  plot will have little effect on the estimate of the number of stages required, as the relative volatility is very high. If a high purity is wanted, say >99 per cent, then reliable data are needed in this region as the equilibrium line approaches the operating line (a pinch point occurs). Of the references cited, none gives values in the region above 95 per cent, and only two give values above 90 per cent; more experimental values are needed to design with confidence. There is a possibility that the system forms an azeotrope in this region. An azeotrope does form at higher pressure, Othmer *et al.* (1952).

## 8.5. PREDICTION OF PHYSICAL PROPERTIES

Whenever possible, experimentally determined values of physical properties should be used. If reliable values cannot be found in the literature and if time, or facilities, are not available for their determination, then in order to proceed with the design the designer must resort to estimation. Techniques are available for the prediction of most physical properties with sufficient accuracy for use in process and equipment design. A detailed review of

all the different methods available is beyond the scope of this book; selected methods are given for the more commonly needed properties. The criterion used for selecting a particular method for presentation in this chapter was to choose the most easily used, simplest, method that had sufficient accuracy for general use. If highly accurate values are required, then specialised texts on physical property estimation should be consulted; such as those by: Reid *et al.* (1987), Poling *et al.* (2000), Bretsznajder (1971) and Sterbacek *et al.* (1979), and AIChE (1983) (1985).

A quick check on the probable accuracy of a particular method can be made by using it to estimate the property for an analogous compound, for which experimental values are available.

The techniques used for prediction are also useful for the correlation, and extrapolation and interpolation, of experimental values.

Group contribution techniques are based on the concept that a particular physical property of a compound can be considered to be made up of contributions from the constituent atoms, groups, and bonds; the contributions being determined from experimental data. They provide the designer with simple, convenient, methods for physical property estimation; requiring only a knowledge of the structural formula of the compound.

Also useful, and convenient to use, are prediction methods based on the use of reduced properties (corresponding states); providing that values for the critical properties are available, or can be estimated with sufficient accuracy; see Sterbacek *et al.* (1979).

## 8.6. DENSITY

### 8.6.1. Liquids

Values for the density of pure liquids can usually be found in the handbooks. It should be noted that the density of most organic liquids, other than those containing a halogen or other “heavy atom”, usually lies between 800 and 1000 kg/m<sup>3</sup>. Liquid densities are given in Appendix C.

An approximate estimate of the density at the normal boiling point can be obtained from the molar volume (see Table 8.6)

$$\rho_b = \frac{M}{V_m} \quad (8.1)$$

where  $\rho_b$  = density, kg/m<sup>3</sup>,  
 $M$  = molecular mass,  
 $V_m$  = molar volume, m<sup>3</sup>/kmol.

For mixtures, it is usually sufficient to take the specific volume of the components as additive; even for non-ideal solutions, as is illustrated by Example 8.1.

The densities of many aqueous solutions are given by Perry *et al.* (1997).

### Example 8.1

Calculate the density of a mixture of methanol and water at 20°C, composition 40 per cent w/w methanol.

Density of water at 20°C	998.2 kg/m <sup>3</sup>
Density of methanol at 20°C	791.2 kg/m <sup>3</sup>

**Solution**

Basis: 1000 kg

$$\text{Volume of water} = \frac{0.6 \times 1000}{998.2} = 0.601 \text{ m}^3$$

$$\text{Volume of methanol} = \frac{0.4 \times 1000}{791.2} = 0.506 \text{ m}^3$$

Total  $1.107 \text{ m}^3$

$$\text{Density of mixture} = \frac{1000}{1.107} = \underline{\underline{903.3 \text{ kg/m}^3}}$$

$$\text{Experimental value} = 934.5 \text{ kg/m}^3$$

$$\text{Error} = \frac{934.5 - 903.3}{903.3} = 3 \text{ per cent, which would be acceptable for most engineering purposes}$$

If data on the variation of density with temperature cannot be found, they can be approximated for non-polar liquids from Smith's equation for thermal expansion (Smith *et al.*, 1954).

$$\beta = \frac{0.04314}{(T_c - T)^{0.641}} \quad (8.2)$$

where  $\beta$  = coefficient of thermal expansion,  $\text{K}^{-1}$ ,

$T_c$  = critical temperature, K,

$T$  = temperature, K.

**8.6.2. Gas and vapour density (specific volume)**

For general engineering purposes it is often sufficient to consider that real gases, and vapours, behave ideally, and to use the gas law:

$$PV = nRT \quad (8.3)$$

where  $P$  = absolute pressure  $\text{N/m}^2$  (Pa),

$V$  = volume  $\text{m}^3$ ,

$n$  = mols of gas

$T$  = absolute temperature, K,

$R$  = universal gas constant,  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  (or  $\text{kJ K}^{-1} \text{ kmol}^{-1}$ ).

$$\text{Specific volume} = \frac{RT}{P} \quad (8.4)$$

These equations will be sufficiently accurate up to moderate pressures, in circumstances where the value is not critical. If greater accuracy is needed, the simplest method is to modify equation 8.3 by including the compressibility factor  $z$ :

$$PV = znRT \quad (8.5)$$

The compressibility factor can be estimated from a generalised compressibility plot, which gives  $z$  as a function of reduced pressure and temperature (Chapter 3, Figure 3.8).

For mixtures, the pseudocritical properties of the mixture should be used to obtain the compressibility factor.

$$P_{c,m} = P_{c,a}y_a + P_{c,b}y_b + \dots \quad (8.6)$$

$$T_{c,m} = T_{c,a}y_a + T_{c,b}y_b + \dots \quad (8.7)$$

where  $P_c$  = critical pressure,

$T_c$  = critical temperature,

$y$  = mol fraction,

suffixes

m = mixture

$a, b$ , etc. = components

## 8.7. VISCOSITY

Viscosity values will be needed for any design calculations involving the transport of fluids or heat. Values for pure substances can usually be found in the literature; see Yaws (1993–1994). Liquid viscosities are given in Appendix C. Methods for the estimation of viscosity are given below.

### 8.7.1. Liquids

A rough estimate of the viscosity of a pure liquid at its boiling point can be obtained from the modified Arrhenius equation:

$$\mu_b = 0.01\rho_b^{0.5} \quad (8.8)$$

where  $\mu_b$  = viscosity, mNs/m<sup>2</sup>,

$\rho_b$  = density at boiling point, kg/m<sup>3</sup>.

A more accurate value can be obtained if reliable values of density are available, or can be estimated with sufficient accuracy, from Souders' equation, Souders (1938):

$$\log(\log 10\mu) = \frac{I}{M}\rho \times 10^{-3} - 2.9 \quad (8.9)$$

where  $\mu$  = viscosity, mNs/m<sup>2</sup>,

$M$  = molecular mass,

$I$  = Souders' index, estimated from the group contributions given in Table 8.1,

$\rho$  = density at the required temperature, kg/m<sup>3</sup>.

### Example 8.2

Estimate the viscosity of toluene at 20°C.

#### Solution

Toluene

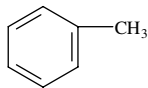


Table 8.1. Contributions for calculating the viscosity constant I in Souders' equation

Atom	H	O	C	N	Cl	Br	I
Contribution	+2.7	+29.7	+50.2	+37.0	+60	+79	+110
Contributions of groups and bonds							
Double bond		-15.5		$\text{H}-\text{C}-\text{R}$ $\parallel$ $\text{O}$			+10
Five-member ring		-24					
Six-member ring		-21					
Side groups on a six-member ring:				$-\text{CH}=\text{CH}-\text{CH}_2-\text{X}^\dagger$			+4
Molecular weight < 17		-9		$\begin{array}{c} \text{R} \\ \diagdown \\ \text{CH}-\text{X} \\ \diagup \\ \text{R} \end{array}$			+6
Molecular weight > 16		-17					
<i>Ortho</i> or <i>para</i> position		+3					
<i>Meta</i> position		-1					
$\begin{array}{c} \text{R} \quad \quad \text{R} \\ \diagdown \quad \diagup \\ \text{CH}-\text{CH} \\ \diagup \quad \diagdown \\ \text{R} \quad \quad \text{R} \end{array}$		+8		OH			+57.1
				COO			+90
				COOH			+104.4
				NO <sub>2</sub>			+80
$\begin{array}{c} \text{R} \\   \\ \text{R}-\text{C}-\text{R} \\   \\ \text{R} \end{array}$		+10					
$-\text{CH}_2-$		+55.6					

<sup>†</sup>X is a negative group.

Contributions from Table 8.1:

7 carbon atoms	$7 \times 50.2 = 351.4$
8 hydrogen atoms	$8 \times 2.7 = 21.6$
3 double bonds	$3(-15.5) = -46.5$
1 six-membered ring	-21.1
1 side group	-9.0
Total, I	$= 296.4$

Density at 20°C = 866 kg/m<sup>3</sup>

Molecular weight 92

$$\log(\log 10\mu) = \frac{296.4 \times 866 \times 10^{-3}}{92} - 2.9 = -0.11$$

$$\log 10\mu = 0.776$$

$$\mu = 0.597, \text{ rounded } = 0.6 \text{ mNs/m}^2$$

experimental value, 0.6 cp = 0.6 mNs/m<sup>2</sup>

*Author's note:* the fit obtained in this example is rather fortuitous, the usual accuracy of the method for organic liquids is around  $\pm 10$  per cent.

### Variation with temperature

If the viscosity is known at a particular temperature, the value at another temperature can be estimated with reasonable accuracy (within  $\pm 20$  per cent) by using the generalised

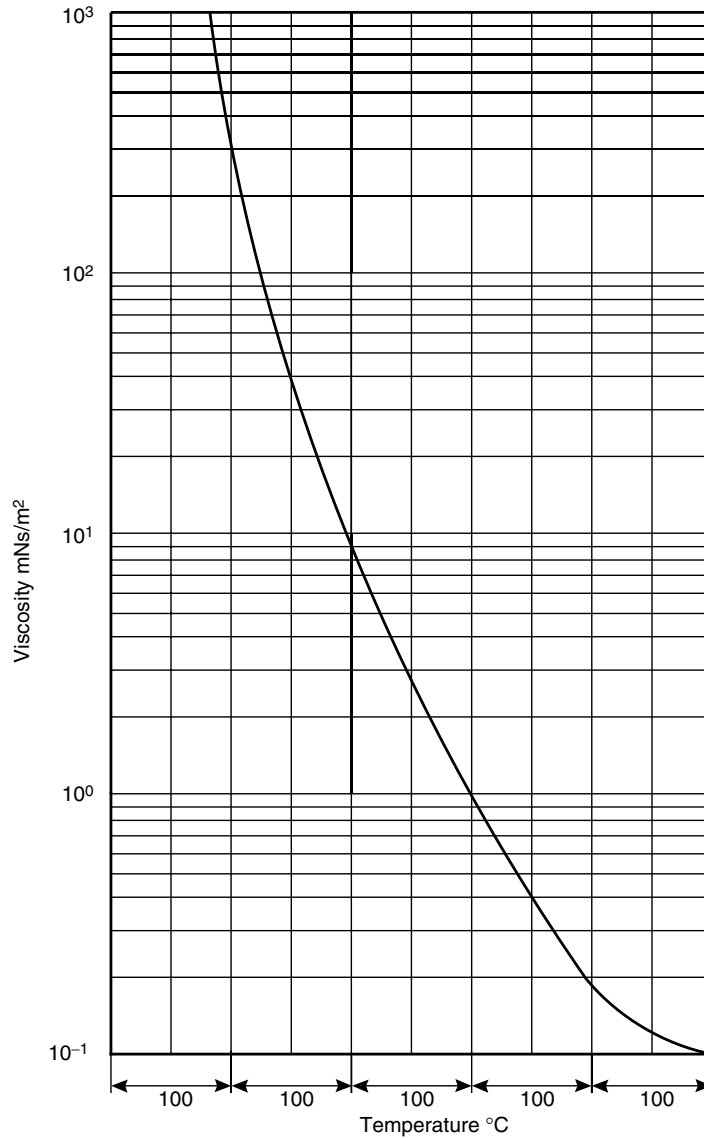


Figure 8.1. Generalised viscosity vs. temperature curve for liquids

plot of Lewis and Squires (1934), Figure 8.1. The scale of the temperature ordinate is obtained by plotting the known value, as illustrated in Example 8.3.

### Example 8.3

Estimate the viscosity of toluene at 80°C, using the value at 20°C given in Example 8.2.

## Solution

Temperature increment  $80 - 20 = 60^\circ\text{C}$ .

From Figure 8.1a, viscosity at  $80^\circ\text{C} = 0.26 \text{ mN s/m}^2$ .

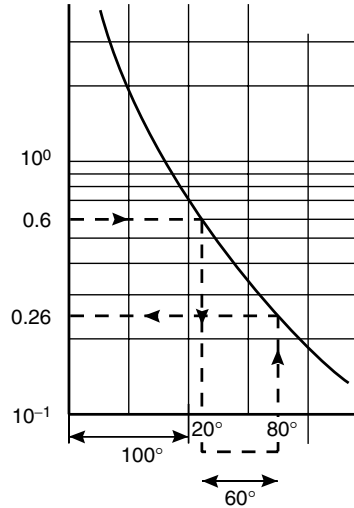


Figure 8.1a.

## Effect of pressure

The viscosity of a liquid is dependent on pressure as well as temperature, but the effect is not significant except at very high pressures. A rise in pressure of 300 bar is roughly equivalent to a decrease in temperature of  $1^\circ\text{C}$ .

## Mixtures

It is difficult to predict the viscosity of mixtures of liquids. Viscosities are rarely additive, and the shape of the viscosity-concentration curve can be complex. The viscosity of the mixture may be lower or, occasionally, higher than that of the pure components. A rough check on the magnitude of the likely error in a design calculation, arising from uncertainty in the viscosity of a mixture, can be made by using the smallest and largest values of the pure components in the calculation, and noting the result.

As an approximation, the variation can be assumed to be linear, if the range of viscosity is not very wide, and a weighted average viscosity calculated. For organic liquid mixtures a modified form of Souders' equation can be used; using a mol fraction weighted average value for the viscosity constant for the mixture  $I_m$ , and the average molecular weight.

For a binary mixture equation 8.9 becomes:

$$\log(\log 10 \mu_m) = \rho_m \left[ \frac{x_1 I_1 + x_2 I_2}{x_1 M_1 + x_2 M_2} \right] \times 10^{-3} - 2.9 \quad (8.10)$$



where  $\mu_m$  = viscosity of mixture,  
 $\rho_m$  = density of mixture,  
 $x_1, x_2$  = mol fraction of components,  
 $M_1, M_2$  = molecular masses of components.

Bretsznajder (1971) gives a detailed review of the methods that have been developed for estimating the viscosity of mixtures, including methods for aqueous solutions and dispersions.

For heat-transfer calculations, Kern (1950) gives a rough rule of thumb for organic liquid mixtures:

$$\frac{1}{\mu_m} = \frac{w_1}{\mu_1} + \frac{w_2}{\mu_2} \quad (8.11)$$

where  $w_1, w_2$  = mass fractions of the components 1 and 2,  
 $\mu_1, \mu_2$  = viscosities of components 1 and 2.

### 8.7.2 Gases

Reliable methods for the prediction of gas viscosities, and the effect of temperature and pressure, are given by Bretsznajder (1971) and Reid *et al.* (1987).

Where an estimate of the viscosity is needed to calculate Prandtl numbers (see Volume 1, Chapter 1) the methods developed for the direct estimation of Prandtl numbers should be used.

For gases at low pressure Bromley (1952) has suggested the following values:

	Prandtl number
Monatomic gases (e.g. Ar, He)	$0.67 \pm 5$ per cent
Non-polar, linear molecules (e.g. O <sub>2</sub> , Cl <sub>2</sub> )	$0.73 \pm 15$ per cent
Non-polar, non-linear molecules (e.g. CH <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> )	$0.79 \pm 15$ per cent
Strongly polar molecules (e.g. CH <sub>3</sub> OH, SO <sub>2</sub> , HCl)	$0.86 \pm 8$ per cent

The Prandtl number for gases varies only slightly with temperature.

## 8.8 THERMAL CONDUCTIVITY

The experimental methods used for the determination of thermal conductivity are described by Tsederberg (1965), who also lists values for many substances. The four-volume handbook by Yaws (1995–1999) is a useful source of thermal conductivity data for hydrocarbons and inorganic compounds.

### 8.8.1. Solids

The thermal conductivity of a solid is determined by its form and structure, as well as composition. Values for the commonly used engineering materials are given in various handbooks.

### 8.8.2. Liquids

The data available in the literature up to 1973 have been reviewed by Jamieson *et al.* (1975). The Weber equation (Weber, 1880) can be used to make a rough estimate of the thermal conductivity of organic liquids, for use in heat-transfer calculations.

$$k = 3.56 \times 10^{-5} C_p \left( \frac{\rho^4}{M} \right)^{1/3} \quad (8.12)$$

where  $k$  = thermal conductivity, W/m°C,

$M$  = molecular mass,

$C_p$  = specific heat capacity, kJ/kg°C,

$\rho$  = density, kg/m<sup>3</sup>.

Bretznajder (1971) gives a group contribution method for estimating the thermal conductivity of liquids.

#### Example 8.4

Estimate the thermal conductivity of benzene at 30°C.

#### Solution

Density at 30°C = 875 kg/m<sup>3</sup>

Molecular mass = 78

Specific heat capacity = 1.75 kJ/kg°C

$$k = 3.56 \times 10^{-5} \times 1.75 \left( \frac{875^4}{78} \right)^{1/3} = \underline{\underline{0.12 \text{ W/m}^\circ\text{C}}} \quad (8.12)$$

Experimental value, 0.16 W/m°C

### 8.8.3. Gases

Approximate values for the thermal conductivity of pure gases, up to moderate pressures, can be estimated from values of the gas viscosity, using Eucken's equation, Eucken (1911):

$$k = \mu \left( C_p + \frac{10.4}{M} \right) \quad (8.13)$$

where  $\mu$  = viscosity, mNs/m<sup>2</sup>,

$C_p$  = specific heat capacity, kJ/kg°C,

$M$  = molecular mass.

#### Example 8.5

Estimate the thermal conductivity of ethane at 1 bar and 450°C.

**Solution**

$$\text{Viscosity} = 0.0134 \text{ mNs/m}^2$$

$$\text{Specific heat capacity} = 2.47 \text{ kJ/kg}^\circ\text{C}$$

$$k = 0.0134 \left( 2.47 + \frac{10.4}{30} \right) = 0.038 \text{ W/m}^\circ\text{C} \quad (8.13)$$

Experimental value, 0.043 W/m<sup>°C</sup>, error 12 per cent.

**8.8.4. Mixtures**

In general, the thermal conductivities of liquid mixtures, and gas mixtures, are not simple functions of composition and the thermal conductivity of the components. Bretsznajder (1971) discusses the methods that are available for estimating the thermal conductivities of mixtures from a knowledge of the thermal conductivity of the components.

If the components are all non-polar a simple weighted average is usually sufficiently accurate for design purposes.

$$k_m = k_1 w_1 + k_2 w_2 + \dots \quad (8.14)$$

where  $k_m$  = thermal conductivity of mixture,

$k_1, k_2$  = thermal conductivity of components,

$w_1, w_2$  = component mass fractions.

**8.9. SPECIFIC HEAT CAPACITY**

The specific heats of the most common organic and inorganic materials can usually be found in the handbooks.

**8.9.1. Solids and liquids**

Approximate values can be calculated for solids, and liquids, by using a modified form of Kopp's law, which is given by Werner (1941). The heat capacity of a compound is taken as the sum of the heat capacities of the individual elements of which it is composed. The values attributed to each element, for liquids and solids, at room temperature, are given in Table 8.2; the method illustrated in Example 8.6.

Table 8.2. Heat capacities of the elements, J/mol<sup>°C</sup>

Element	Solids	Liquids
C	7.5	11.7
H	9.6	18.0
B	11.3	19.7
Si	15.9	24.3
O	16.7	25.1
F	20.9	29.3
P and S	22.6	31.0
all others	26.0	33.5

**Example 8.6**

Estimate the specific heat capacity of urea,  $\text{CH}_4\text{N}_2\text{O}$ .

**Solution**

Element	mol. mass	Heat capacity
C	12	$7.5 = 7.5$
H	4	$4 \times 9.6 = 38.4$
N	28	$2 \times 26.0 = 52.0$
O	16	$16.7 = 16.7$
	<hr style="width: 50%; margin-left: 0;"/>	<hr style="width: 50%; margin-left: 0;"/>
	60	114.6 J/mol°C

$$\text{Specific heat capacity} = \frac{114.6}{60} = \underline{\underline{1.91 \text{ J/g}^\circ\text{C}}} \text{ (kJ/kg}^\circ\text{C)}$$

Experimental value 1.34 kJ/kg°C.

Kopp's rule does not take into account the arrangement of the atoms in the molecule, and, at best, gives only very approximate, "ball-park" values.

For organic liquids, the group contribution method proposed by Chueh and Swanson (1973a,b) will give accurate predictions. The contributions to be assigned to each molecular group are given in Table 8.3 and the method illustrated in Examples 8.7 and 8.8.

Liquid specific heats do not vary much with temperature, at temperatures well below the critical temperature (reduced temperature  $< 0.7$ ).

The specific heats of liquid mixtures can be estimated, with sufficient accuracy for most technical calculations, by taking heat capacities of the components as additive.

For dilute aqueous solutions it is usually sufficient to take the specific heat of the solution as that of water.

**Example 8.7**

Using Chueh and Swanson's method, estimate the specific heat capacity of ethyl bromide at 20°C.

**Solution**

Ethyl bromide  $\text{CH}_3\text{CH}_2\text{Br}$

Group	Contribution	No. of
—CH <sub>3</sub>	36.84	1 = 36.84
—CH <sub>2</sub> —	30.40	1 = 30.40
—Br	37.68	1 = 37.68
		<hr style="width: 50%; margin-left: 0;"/>
		Total 104.92 kJ/kmol°C

Table 8.3. Group contributions for liquid heat capacities at 20°C, kJ/kmol°C (Chueh and Swanson, 1973a, b)

Group	Value	Group	Value
Alkane	—CH <sub>3</sub> —CH <sub>2</sub> — —CH— —C—	$\begin{array}{c} \text{O} \\    \\ \text{—C—O—} \end{array}$	60.71
		—CH <sub>2</sub> OH	73.27
		$\begin{array}{c}   \\ \text{—CHOH} \end{array}$	76.20
		$\begin{array}{c}   \\ \text{—COH} \\   \\ \text{—OH} \end{array}$	111.37
Olefin	=CH <sub>2</sub> =C—H =C—	—ONO <sub>2</sub>	44.80
			119.32
		Halogen	
Alkyne	—C≡H —C≡	—Cl (first or second on a carbon)	36.01
		—Cl (third or fourth on a carbon)	25.12
		—Br	37.68
		—F	16.75
In a ring	—CH=	—I	36.01
		Nitrogen	
		$\begin{array}{c} \text{H} \\   \\ \text{H—N—} \end{array}$	58.62
Oxygen	—C≡ or —C— —C=	$\begin{array}{c} \text{H} \\   \\ \text{—N—} \\   \\ \text{—N—} \end{array}$	43.96
		—N—	31.40
		—N=(in a ring)	18.84
		—C≡N	58.70
Oxygen	—O— $\begin{array}{c} \diagdown \\ \text{C=O} \\ \diagup \end{array}$ —C—O H $\begin{array}{c} \text{O} \\    \\ \text{—C—OH} \end{array}$	Sulphur	
		—SH	44.80
		—S—	33.49
		Hydrogen	
		H— (for formic acid, formates, hydrogen cyanide, etc.)	14.65

Add 18.84 for any carbon group which fulfils the following criterion: a carbon group which is joined by a single bond to a carbon group connected by a double or triple bond with a third carbon group. In some cases a carbon group fulfils the above criterion in more ways than one; 18.84 should be added each time the group fulfils the criterion.

Exceptions to the above 18.84 rule:

1. No such extra 18.84 additions for —CH<sub>3</sub> groups.
2. For a —CH<sub>2</sub>— group fulfilling the 18.84 addition criterion add 10.47 instead of 18.84. However, when the —CH<sub>2</sub>— group fulfils the addition criterion in more ways than one, the addition should be 10.47 the first time and 18.84 for each subsequent addition.
3. No such extra addition for any carbon group in a ring.

mol. wt. = 109

$$\text{Specific heat capacity} = \frac{104.92}{109} = \underline{\underline{0.96 \text{ kJ/kg}^\circ\text{C}}}$$

Experimental value 0.90 kJ/kg°C

### Example 8.8

Estimate the specific heat capacity of chlorobutadiene at 20°C, using Chueh and Swanson's method.

### Solution

Structural formula  $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$ , mol. wt. 88.5



Group	Contribution	No. of	Addition rule	Total
$=\text{CH}_2$	21.77	2	—	= 43.54
$=\text{C}-$	15.91	1	18.84	= 34.75
$\begin{array}{c}   \\   \\ =\text{CH} \end{array}$	21.35	1	18.84	= 40.19
$-\text{Cl}$	36.01	1	—	= 36.01
				<u>154.49</u> kJ/kmol°C

$$\text{Specific heat capacity} = \frac{154.49}{88.5} = \underline{\underline{1.75 \text{ kJ/kg}^\circ\text{C}}}$$

### 8.9.2. Gases

The dependence of gas specific heats on temperature was discussed in Chapter 3, Section 3.5. For a gas in the ideal state the specific heat capacity at constant pressure is given by:

$$C_p^\circ = a + bT + cT^2 + dT^3 \quad (\text{equation 3.19})$$

Values for the constants in this equation for the more common gases can be found in the handbooks, and in Appendix C.

Several group contribution methods have been developed for the estimation of the constants, such as that by Rihani and Doraiswamy (1965) for organic compounds. Their values for each molecular group are given in Table 8.4, and the method illustrated in Example 8.9. The values should not be used for acetylenic compounds.

The correction of the ideal gas heat capacity to account for real conditions of temperature and pressure was discussed in Chapter 3, Section 3.7.

Table 8.4. Group contributions to ideal gas heat capacities, kJ/kmol°C (Rihani and Doraiswamy, 1965)




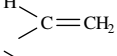
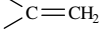
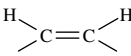
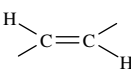
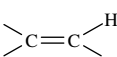
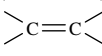
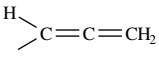
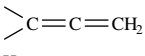
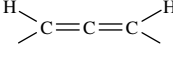





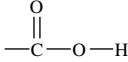
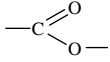





Group	<i>a</i>	<i>b</i> × 10 <sup>2</sup>	<i>c</i> × 10 <sup>4</sup>	<i>d</i> × 10 <sup>6</sup>
Aliphatic hydrocarbon groups				
—CH <sub>3</sub>	2.5485	8.9740	-0.3567	0.004752
	1.6518	8.9447	-0.5012	0.0187
=CH <sub>2</sub>	2.2048	7.6857	-0.3994	0.008264
	-14.7516	14.3020	-1.1791	0.03356
	-24.4131	18.6493	-1.7619	0.05288
	1.1610	14.4786	-0.8031	0.01792
	-1.7472	16.2694	-1.1652	0.03083
	-13.0676	15.9356	-0.9877	0.02305
	3.9261	12.5208	-0.7323	0.01641
	-6.161	14.1696	-0.9927	0.02594
	1.9829	14.7304	-1.3188	0.03854
	9.3784	17.9597	-1.07433	0.02474
	11.0146	17.4414	-1.1912	0.03047
	-13.0833	20.8878	-1.8018	0.05447
Aromatic hydrocarbon groups				
	-6.1010	8.0165	-0.5162	0.01250
	-5.8125	6.3468	-0.4476	0.01113
	0.5104	5.0953	-0.3580	0.00888
Contributions due to ring formation				
Three-membered ring	-14.7878	-0.1256	0.3129	-0.02309
Four-membered ring	-36.2368	4.5134	0.1779	-0.00105
Five-membered ring:				
Pentane	-51.4348	7.7913	-0.4342	0.00898
Pentene	-28.8106	3.2732	-0.1445	0.00247
Six-membered ring:				
Hexane	-56.0709	8.9564	-0.1796	-0.00781
Hexene	-33.5941	9.3110	-0.80118	0.02291

Table 8.4. (continued)

Group	<i>a</i>	<i>b</i> × 10 <sup>2</sup>	<i>c</i> × 10 <sup>4</sup>	<i>d</i> × 10 <sup>6</sup>
Oxygen-containing groups				
—OH	27.2691	−0.5640	0.1733	−0.00680
—O—	11.9161	−0.04187	0.1901	−0.01142
	14.7308	3.9511	0.2571	−0.02922
	4.1935	8.6931	−0.6850	0.01882
	5.8846	14.4997	−1.0706	0.02883
	11.4509	4.5012	0.2793	−0.03864
	−15.6352	5.7472	−0.5296	0.01586
Nitrogen-containing groups				
—C≡N	18.8841	2.2864	0.1126	−0.01587
—N≡C	21.2941	1.4620	0.1084	−0.01020
—NH <sub>2</sub>	17.4937	3.0890	0.2843	−0.03061
	−5.2461	9.1825	−0.6716	0.01774
	−14.5186	12.3230	−1.1191	0.03277
	10.2401	1.4386	0.07159	−0.01138
—NO <sub>2</sub>	4.5638	11.0536	−0.7834	0.01989
Sulphur-containing groups				
—SH	10.7170	5.5881	−0.4978	0.01599
—S—	17.6917	0.4719	−0.0109	−0.00030
	17.0922	−0.1260	0.3061	−0.02546
—SO <sub>3</sub> H	28.9802	10.3561	0.7436	−0.09397
Halogen-containing groups				
—F	6.0215	1.4453	−0.0444	−0.00014
—Cl	12.8373	0.8885	−0.0536	0.00116
—Br	11.5577	1.9808	−0.1905	0.0060
—I	13.6703	2.0520	−0.2257	0.00746

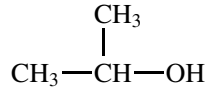


**Example 8.9**

Estimate the specific heat capacity of isopropyl alcohol at 500 K.

**Solution**

Structural formula



Group	No. of	$a$	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
—CH <sub>3</sub>	2	5.0970	17.9480	−0.7134	0.0095
— $\begin{array}{c}   \\ \text{CH} \\   \end{array}$	1	−14.7516	14.3020	−1.1791	0.03356
—OH	1	27.2691	−0.5640	0.1733	−0.0068
Total		17.6145	31.6860	−1.7190	0.0363

$$C_p^\circ = 17.6145 + 31.6860 \times 10^{-2}T - 1.7192 \times 10^{-4}T^2 + 0.0363 \times 10^{-6}T^3.$$

At 500 K, substitution gives:

$$C_p = \underline{\underline{137.6 \text{ kJ/kmol}^\circ\text{C}}}$$

Experimental value, 31.78 cal/mol $^\circ\text{C}$  = 132.8 kJ/kmol $^\circ\text{C}$ , error 4 per cent.

**8.10. ENTHALPY OF VAPORISATION (LATENT HEAT)**

The latent heats of vaporisation of the more commonly used materials can be found in the handbooks and in Appendix C.

A very rough estimate can be obtained from Trouton's rule (Trouton, 1884), one of the oldest prediction methods.

$$\frac{L_v}{T_b} = \text{constant} \quad (8.15)$$

where  $L_v$  = latent heat of vaporisation, kJ/kmol,

$T_b$  = normal boiling point, K.

For organic liquids the constant can be taken as 100.

More accurate estimates, suitable for most engineering purposes, can be made from a knowledge of the vapour pressure-temperature relationship for the substance. Several correlations have been proposed; see Reid *et al.* (1987).

The equation presented here, due to Haggemacher (1946), is derived from the Antoine vapour pressure equation (see Section 8.11).

$$L_v = \frac{8.32 BT^2 \Delta z}{(T + C)^2} \quad (8.16)$$

where  $L_v$  = latent heat at the required temperature, kJ/kmol,

$T$  = temperature, K,

$B, C$  = coefficients in the Antoine equation (equation 8.20),

$\Delta z = z_{\text{gas}} - z_{\text{liquid}}$  (where  $z$  is the compressibility constant), calculated from the equation:

$$\Delta z = \left[ 1 - \frac{P_r}{T_r^3} \right]^{0.5} \quad (8.17)$$

$P_r$  = reduced pressure,

$T_r$  = reduced temperature.

If an experimental value of the latent heat at the boiling point is known, the Watson equation (Watson, 1943), can be used to estimate the latent heat at other temperatures.

$$L_v = L_{v,b} \left[ \frac{T_c - T}{T_c - T_b} \right]^{0.38} \quad (8.18)$$

where  $L_v$  = latent heat at temperature  $T$ , kJ/kmol,

$L_{v,b}$  = latent heat at the normal boiling point, kJ/kmol,

$T_b$  = boiling point, K,

$T_c$  = critical temperature, K,

$T$  = temperature, K.

Over a limited range of temperature, up to 100°C, the variation of latent heat with temperature can usually be taken as linear.

### 8.10.1. Mixtures

For design purposes it is usually sufficiently accurate to take the latent heats of the components of a mixture as additive:

$$L_v \text{ mixture} = L_{v1}x_1 + L_{v2}x_2 + \dots \quad (8.19)$$

where  $L_{v1}, L_{v2}$  = latent heats of the components kJ/kmol,

$x_1, x_2$  = mol fractions of components.

### Example 8.10

Estimate the latent heat of vaporisation of acetic anhydride,  $\text{C}_4\text{H}_6\text{O}_3$ , at its boiling point, 139.6°C (412.7 K), and at 200°C (473 K).

### Solution

For acetic anhydride  $T_c = 569.1$  K,  $P_c = 46$  bar,

Antoine constants  $A = 16.3982$

$B = 3287.56$

$C = -75.11$

Experimental value at the boiling point 41,242 kJ/kmol.

From Trouton's rule:

$$L_{v,b} = 100 \times 412.7 = \underline{\underline{41,270 \text{ kJ/kmol}}}$$

*Note:* the close approximation to the experimental value is fortuitous, the rule normally gives only a very approximate estimate.

From Haggemacher's equation:

$$\text{at the b.p. } P_r = \frac{1}{46} = 0.02124$$

$$T_r = \frac{412.7}{569.1} = 0.7252$$

$$\Delta z = \left[ 1 - \frac{0.02124}{0.7252^3} \right]^{0.5} = 0.972$$

$$L_{v,b} = \frac{8.32 \times 3287.6 \times (412.7)^2 \times 0.972}{(412.7 - 75.11)^2} = \underline{\underline{39,733 \text{ kJ/mol}}}$$

At 200°C, the vapour pressure must first be estimated, from the Antoine equation:

$$\ln P = A - \frac{B}{T + C}$$

$$\ln P = 16.3982 - \frac{3287.56}{473 - 75.11} = 8.14$$

$$P = 3421.35 \text{ mmHg} = 4.5 \text{ bar}$$

$$P_c = \frac{4.5}{46} = 0.098$$

$$T_c = \frac{473}{569.1} = 0.831$$

$$\Delta z = \left[ 1 - \frac{0.098}{0.831^3} \right]^{0.5} = 0.911$$

$$L_v = \frac{8.32 \times 3287.6 \times (473)^2 \times 0.911}{(473 - 75.11)^2} = \underline{\underline{35,211 \text{ kJ/kmol}}}$$

Using Watson's equation and the experimental value at the b.p.

$$L_v = 41,242 \left[ \frac{569.1 - 473}{569.1 - 412.7} \right]^{0.38} = \underline{\underline{34,260 \text{ kJ/kmol}}}$$

## 8.11. VAPOUR PRESSURE

If the normal boiling point (vapour pressure = 1 atm) and the critical temperature and pressure are known, then a straight line drawn through these two points on a plot of log-pressure versus reciprocal absolute temperature can be used to make a rough estimation of the vapour pressure at intermediate temperatures.

Several equations have been developed to express vapour pressure as a function of temperature. One of the most commonly used is the three-term Antoine equation, Antoine (1888):

$$\ln P = A - \frac{B}{T + C} \quad (8.20)$$

where  $P$  = vapour pressure, mmHg,  
 $A, B, C$  = the Antoine coefficients,  
 $T$  = temperature, K.

Vapour pressure data, in the form of the constants in the Antoine equation, are given in several references; the compilations by Ohe (1976), Dreisbach (1952), Hala *et al.* (1968) and Hirata *et al.* (1975) give values for several thousand compounds. Antoine vapour pressure coefficients for the elements are given by Nesmeyanov (1963). Care must be taken when using Antoine coefficients taken from the literature in equation 8.20, as the equation is often written in different and ambiguous forms; the logarithm of the pressure may be to the base 10, instead of the natural logarithm, and the temperature may be degrees Celsius, not absolute temperature. Also, occasionally, the minus sign shown in equation 8.20 is included in the constant  $B$  and the equation written with a plus sign. The pressure may also be in units other than mm Hg. Always check the actual form of the equation used in the particular reference. Antoine constants for use in equation 8.20 are given in Appendix C. Vapour pressure data for hydrocarbons can be found in the four-volume handbook by Yaws (1994–1995).

## 8.12. DIFFUSION COEFFICIENTS (DIFFUSIVITIES)

Diffusion coefficients are needed in the design of mass transfer processes; such as gas absorption, distillation and liquid-liquid extraction.

Experimental values for the more common systems can be often found in the literature, but for most design work the values will have to be estimated. Methods for the prediction of gas and liquid diffusivities are given in Volume 1, Chapter 10; some experimental values are also given.

### 8.12.1. Gases

The equation developed by Fuller *et al.* (1966) is easy to apply and gives reliable estimates:

$$D_v = \frac{1.013 \times 10^{-7} T^{1.75} \left( \frac{1}{M_a} + \frac{1}{M_b} \right)^{1/2}}{P \left[ \left( \sum_a v_i \right)^{1/3} + \left( \sum_b v_i \right)^{1/3} \right]^2} \quad (8.21)$$

where  $D_v$  = diffusivity, m<sup>2</sup>/s,  
 $T$  = temperature, K,  
 $M_a, M_b$  = molecular masses of components  $a$  and  $b$ ,  
 $P$  = total pressure, bar,

$\sum_a v_i, \sum_b v_i$  = the summation of the special diffusion volume coefficients for components  $a$  and  $b$ , given in Table 8.5.

The method is illustrated in Example 8.11.

Table 8.5. Special atomic diffusion volumes (Fuller *et al.*, 1966)

Atomic and structural diffusion volume increments			
C	16.5	Cl	19.5*
H	1.98	S	17.0*
O	5.48	Aromatic or hetrocyclic rings	-20.0
N	5.69*		

Diffusion volumes of simple molecules

H <sub>2</sub>	7.07	CO	18.9
D <sub>2</sub>	6.70	CO <sub>2</sub>	26.9
He	2.88	N <sub>2</sub> O	35.9
N <sub>2</sub>	17.9	NH <sub>3</sub>	14.9
O <sub>2</sub>	16.6	H <sub>2</sub>	12.7
Air	20.1	CCL <sub>2</sub> F <sub>2</sub>	114.8*
Ne	5.59	SF <sub>6</sub>	69.7*
Ar	16.1	Cl <sub>2</sub>	37.7*
Kr	22.8	Br <sub>2</sub>	67.2*
Xe	37.9*	SO <sub>2</sub>	41.1*

\*Value based on only a few data points

### Example 8.11

Estimate the diffusivity of methanol in air at atmospheric pressure and 25°C.

### Solution

Diffusion volumes from Table 8.5; methanol:

Element	$v_i$		No. of	
C	16.50	×	1	= 16.50
H	1.98	×	4	= 7.92
O	5.48	×	1	= 5.48
			$\sum_a v_i$	<u>29.90</u>

Diffusion volume for air = 20.1.

1 standard atmosphere = 1.013 bar.

molecular mass CH<sub>3</sub>OH = 32, air = 29.

$$D_v = \frac{1.013 \times 10^{-7} \times 298^{1.75} (1/32 + 1/29)^{1/2}}{1.013 [(29.90)^{1/3} + (20.1)^{1/3}]^2} \quad (8.21)$$

$$= \underline{\underline{16.2 \times 10^{-6} \text{ m}^2/\text{s}}}$$

Experimental value,  $15.9 \times 10^{-6} \text{ m}^2/\text{s}$ .

### 8.12.2. Liquids

The equation developed by Wilke and Chang (1955), given below, can be used to predict liquid diffusivity. This equation is discussed in Volume 1, Chapter 10.

$$D_L = \frac{1.173 \times 10^{-13} (\phi M)^{0.5} T}{\mu V_m^{0.6}} \quad (8.22)$$

where  $D_L$  = liquid diffusivity,  $\text{m}^2/\text{s}$ ,

$\phi$  = an association factor for the solvent,

= 2.6 for water (some workers recommend 2.26),

= 1.9 for methanol,

= 1.5 for ethanol,

= 1.0 for unassociated solvents,

$M$  = molecular mass of solvent,

$\mu$  = viscosity of solvent,  $\text{mN s/m}^2$ ,

$T$  = temperature, K,

$V_m$  = molar volume of the solute at its boiling point,  $\text{m}^3/\text{kmol}$ . This can be estimated from the group contributions given in Table 8.6.

The method is illustrated in Example 8.12.

The Wilke-Chang correlation is shown graphically in Figure 8.2. This figure can be used to determine the association constant for a solvent from experimental values for  $D_L$  in the solvent.

The Wilke-Chang equation gives satisfactory predictions for the diffusivity of organic compounds in water but not for water in organic solvents.


#### Example 8.12

Estimate the diffusivity of phenol in ethanol at  $20^\circ\text{C}$  (293 K).

#### Solution

Viscosity of ethanol at  $20^\circ\text{C}$ ,  $1.2 \text{ mNs/m}^2$ .

Molecular mass, 46.

Molar volume of phenol  from Table 8.6:

Atom	Vol.		No. of		
C	0.0148	×	6	=	0.0888
H	0.0037	×	6	=	0.0222
O	0.0074	×	1	=	0.0074
ring	-0.015	×	1	=	-0.015
					<hr style="width: 100px; margin-left: auto; margin-right: 0;"/>
					0.1034 $\text{m}^3/\text{k mol}$

$$D_L = \frac{1.173 \times 10^{-13} (1.5 \times 46)^{0.5} 293}{1.2 \times 0.1034^{0.6}} = \underline{\underline{9.28 \times 10^{-10} \text{ m}^2/\text{s}}} \quad (8.22)$$

Experimental value,  $8 \times 10^{-10} \text{ m}^2/\text{s}$

Table 8.6. Structural contributions to molar volumes, m<sup>3</sup>/kmol (Gambil, 1958)

Molecular volumes							
Air	0.0299	CO <sub>2</sub>	0.0340	H <sub>2</sub> S	0.0329	NO	0.0236
Br <sub>2</sub>	0.0532	COS	0.0515	I <sub>2</sub>	0.0715	N <sub>2</sub> O	0.0364
Cl <sub>2</sub>	0.0484	H <sub>2</sub>	0.0143	N <sub>2</sub>	0.0312	O <sub>2</sub>	0.0256
CO	0.0307	H <sub>2</sub> O	0.0189	NH <sub>3</sub>	0.0258	SO <sub>2</sub>	0.0448
Atomic volumes							
As	0.0305	F	0.0087	P	0.0270	Sn	0.0423
Bi	0.0480	Ge	0.0345	Pb	0.0480	Ti	0.0357
Br	0.0270	H	0.0037	S	0.0256	V	0.0320
C	0.0148	Hg	0.0190	Sb	0.0342	Zn	0.0204
Cr	0.0274	I	0.037	Si	0.0320		

Cl, terminal, as in RCl	0.0216	in higher esters, ethers	0.0110
medial, as in R—CHCl—R	0.0246	in acids	0.0120
Nitrogen, double-bonded	0.0156	in union with S, P, N	0.0083
triply bonded, as in nitriles	0.0162	three-membered ring	-0.0060
in primary amines, RNH <sub>2</sub>	0.0105	four-membered ring	-0.0085
in secondary amines, R <sub>2</sub> NH	0.012	five-membered ring	-0.0115
in tertiary amines, R <sub>3</sub> N	0.0108	six-membered ring as in benzene, cyclohexane, pyridine	-0.0150
Oxygen, except as noted below	0.0074		
in methyl esters	0.0091	Naphthalene ring	-0.0300
in methyl ethers	0.0099	Anthracene ring	-0.0475

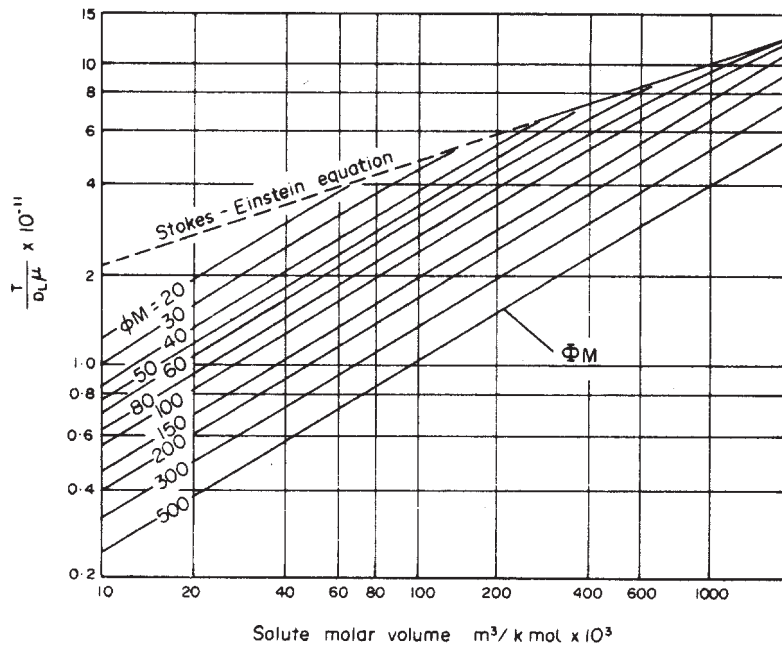


Figure 8.2. The Wilke-Chang correlation

### 8.13. SURFACE TENSION

It is usually difficult to find experimental values for surface tension for any but the more commonly used liquids. A useful compilation of experimental values is that by Jasper (1972), which covers over 2000 pure liquids. Othmer *et al.* (1968) give a nomograph covering about 100 compounds.

If reliable values of the liquid and vapour density are available, the surface tension can be estimated from the Sugden parachor; which can be estimated by a group contribution method, Sugden (1924).

$$\sigma = \left[ \frac{P_{ch}(\rho_L - \rho_v)}{M} \right]^4 \times 10^{-12} \quad (8.23)$$

where  $\sigma$  = surface tension, mJ/m<sup>2</sup> (dyne/cm),

$P_{ch}$  = Sugden's parachor,

$\rho_L$  = liquid density, kg/m<sup>3</sup>,

$\rho_v$  = density of the saturated vapour, kg/m<sup>3</sup>,

$M$  = molecular mass.

$\sigma$ ,  $\rho_L$ ,  $\rho_v$  evaluated at the system temperature.

The vapour density can be neglected when it is small compared with the liquid density.

The parachor can be calculated using the group contributions given in Table 8.7. The method is illustrated in Example 8.13.

Table 8.7. Contribution to Sugden's parachor for organic compounds (Sugden, 1924)

Atom, group or bond	Contribution	Atom, group or bond	Contribution
C	4.8	Si	25.0
H	17.1	Al	38.6
H in (OH)	11.3	Sn	57.9
O	20.0	As	50.1
O <sub>2</sub> in esters, acids	60.0	Double bond: terminal	
N	12.5	2,3-position	23.2
S	48.2	3,4-position	
P	37.7	Triple bond	46.6
F	25.7	Rings	
Cl	54.3	3-membered	16.7
Br	68.0	4-membered	11.6
I	91.0	5-membered	8.5
Se	62.5	6-membered	6.1

#### 8.13.1. Mixtures

The surface tension of a mixture is rarely a simple function of composition. However, for hydrocarbons a rough value can be calculated by assuming a linear relationship.

$$\sigma_m = \sigma_1 x_1 + \sigma_2 x_2 \dots \quad (8.24)$$

where  $\sigma_m$  = surface tension of mixture,

$\sigma_1$ ,  $\sigma_2$  = surface tension of components,

$x_1$ ,  $x_2$  = component mol fractions.



**Example 8.13**

Estimate the surface tension of pure methanol at 20°C, density 791.7 kg/m<sup>3</sup>, molecular weight 32.04.

**Solution**

Calculation of parachor, CH<sub>3</sub>OH, Table 8.7.

Group	Contribution	No.
C	4.8	× 1 = 4.8
H–O	11.3	× 1 = 11.3
H–C	17.1	× 3 = 51.3
O	20.0	× 1 = 20.0
		87.4

$$\sigma = \left[ \frac{87.4 \times 791.7}{32.04} \right]^4 \times 10^{-12} = \underline{\underline{21.8 \text{ mJ/m}^2}} \quad (8.23)$$

Experimental value 22.5 mJ/m<sup>2</sup>.

**8.14. CRITICAL CONSTANTS**

Values of the critical temperature and pressure will be needed for prediction methods that correlate physical properties with the reduced conditions. Experimental values for many substances can be found in various handbooks; and in Appendix C. Critical reviews of the literature on critical constants, and summaries of selected values, have been published by Kudchadker *et al.* (1968), for organic compounds, and by Mathews (1972), for inorganic compounds. An earlier review was published by Kobe and Lynn (1953).

If reliable experimental values cannot be found, techniques are available for estimating the critical constants with sufficient accuracy for most design purposes. For organic compounds Lydersen's method is normally used, Lydersen (1955):

$$T_c = \frac{T_b}{[0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2]} \quad (8.25)$$

$$P_c = \frac{M}{(0.34 + \Sigma \Delta P)^2} \quad (8.26)$$

$$V_c = 0.04 + \Sigma \Delta V \quad (8.27)$$

where  $T_c$  = critical temperature, K,

$P_c$  = critical pressure, atm (1.0133 bar),

$V_c$  = molar volume at the critical conditions, m<sup>3</sup>/kmol,

$T_b$  = normal boiling point, K,

$M$  = relative molecular mass,

$\Delta T$  = critical temperature increments, Table 8.8,

$\Delta P$  = critical pressure increments, Table 8.8,

$\Delta V$  = molar volume increments, Table 8.8.

Table 8.8. Critical constant increments (Lydersen, 1955)

	$\Delta T$	$\Delta P$	$\Delta V$		$\Delta T$	$\Delta P$	$\Delta V$
<i>Non-ring increments</i>							
—CH <sub>3</sub>	0.020	0.227	0.055	$\begin{array}{c}   \\ =C- \end{array}$	0.0	0.198	0.036
—CH <sub>2</sub>	0.020	0.227	0.055	=C=	0.0	0.198	0.036
$\begin{array}{c}   \\ -CH \\   \end{array}$	0.012	0.210	0.051	$\begin{array}{c} \equiv CH \\ \equiv C- \end{array}$	0.005	0.153	0.036*
$\begin{array}{c}   \\ -C- \\   \end{array}$	0.00	0.210	0.041	H	0	0	0
=CH <sub>2</sub>	0.018	0.198	0.045				
$\begin{array}{c}   \\ =CH \end{array}$	0.018	0.198	0.045				
<i>Ring increments</i>							
—CH <sub>2</sub> —	0.013	0.184	0.0445	$\begin{array}{c}   \\ =CH \end{array}$	0.011	0.154	0.037
$\begin{array}{c}   \\ -CH \\   \end{array}$	0.012	0.192	0.046	$\begin{array}{c}   \\ =C- \\   \end{array}$	0.011	0.154	0.036
$\begin{array}{c}   \\ -C- \\   \end{array}$	-0.007*	0.154*	0.031*	=C=	0.011	0.154	0.036
<i>Halogen increments</i>							
—F	0.018	0.224	0.018	—Br	0.010	0.50*	0.070*
—Cl	0.017	0.320	0.049	—I	0.012	0.83*	0.095*
<i>Oxygen increments</i>							
—OH (alcohols)	0.082	0.06	0.018*	$\begin{array}{c}   \\ -CO \text{ (ring)} \end{array}$	0.033*	0.2*	0.050*
—OH (phenols)	0.031	-0.02*	0.030*	$\begin{array}{c}   \\ HC=O \text{ (aldehyde)} \end{array}$	0.048	0.33	0.073
—O— (non-ring)	0.021	0.16	0.020	—COOH (acid)	0.085	0.4*	0.080
—O— (ring)	0.014*	0.12*	0.080*	—COO— (ester)	0.047	0.47	0.080
$\begin{array}{c}   \\ -C=O \text{ (non-ring)} \end{array}$	0.040	0.29	0.060	=O (except for combinations above)	0.02*	0.12*	0.011*
<i>Nitrogen increments</i>							
—NH <sub>2</sub>	0.031	0.095	0.028	$\begin{array}{c}   \\ -N- \text{ (ring)} \end{array}$	0.007*	0.013*	0.032*
$\begin{array}{c}   \\ -NH \text{ (non-ring)} \end{array}$	0.031	0.135	0.037*	—CN	0.060*	0.36*	0.080*
$\begin{array}{c}   \\ -NH \text{ (ring)} \end{array}$	0.024*	0.09*	0.027*	—NO <sub>2</sub>	0.055*	0.42*	0.078*
$\begin{array}{c}   \\ -N- \text{ (non-ring)} \end{array}$	0.014	0.17	0.042*				

(continued overleaf)

Table 8.8. (continued)

	$\Delta T$	$\Delta P$	$\Delta V$		$\Delta T$	$\Delta P$	$\Delta V$
<i>Sulphur Increments</i>							
—SH	0.015	0.27	0.055	—S—(ring)	0.008*	0.24*	0.045*
—S—(non-ring)	0.015	0.27	0.055	S	0.003*	0.24*	0.047*
<i>Miscellaneous</i>							
$\begin{array}{c}   \\ \text{—Si—} \\   \end{array}$	0.03	0.54*		$\begin{array}{c}   \\ \text{—B—} \\   \end{array}$		0.03*	

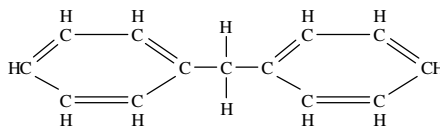
Dashes represent bonds with atoms other than hydrogen.

Values marked with an asterisk are based on too few experimental points to be reliable.

Fedons (1982) gives a simple method for the estimation of critical temperature, that does not require a knowledge of the boiling point of the compound.

### Example 8.14

Estimate the critical constants for diphenylmethane using Lydersen's method; normal boiling point 537.5 K, molecular mass 168.2, structural formula:



### Solution

Group	No. of	Total contribution		
		$\Delta T$	$\Delta P$	$\Delta V$
$\begin{array}{c}    \\ \text{H—C—(ring)} \end{array}$	10	0.11	1.54	0.37
$\begin{array}{c}   \\ =\text{C—(ring)} \end{array}$	2	0.022	0.308	0.072
—CH <sub>2</sub> —	1	0.02	0.227	0.055
	$\Sigma$	0.152	2.075	0.497

$$T_c = \frac{537.5}{(0.567 + 0.152 - 0.152^2)} = \underline{\underline{772 \text{ k}}}$$

experimental value 767 K,

$$P_c = \frac{168.2}{(0.34 + 2.075)^2} = \underline{\underline{28.8 \text{ atm}}}$$

experimental value 28.2 atm,

$$V_c = 0.04 + 0.497 = \underline{\underline{0.537 \text{ m}^3/\text{kmol}}}$$

## 8.15. ENTHALPY OF REACTION AND ENTHALPY OF FORMATION

Enthalpies of reaction (heats of reaction) for the reactions used in the production of commercial chemicals can usually be found in the literature. Stephenson (1966) gives values for most of the production processes he describes in his book.

Heats of reaction can be calculated from the heats of formation of the reactants and products, as described in Chapter 3, Section 3.11. Values of the standard heats of formation for the more common chemicals are given in various handbooks; see also Appendix C. A useful source of data on heats of formation, and combustion, is the critical review of the literature by Domalski (1972).

Benson has developed a detailed group contribution method for the estimation of heats of formation; see Benson (1976) and Benson *et al.* (1968). He estimates the accuracy of the method to be from  $\pm 2.0$  kJ/mol for simple compounds, to about  $\pm 12$  kJ/mol for highly substituted compounds. Benson's method, and other group contribution methods for the estimation of heats of formation, are described by Reid *et al.* (1987).

## 8.16. PHASE EQUILIBRIUM DATA

Phase equilibrium data are needed for the design of all separation processes that depend on differences in concentration between phases.

### 8.16.1. Experimental data

Experimental data have been published for several thousand binary and many multicomponent systems. Virtually all the published experimental data has been collected together in the volumes comprising the DECHEMA vapour-liquid and liquid-liquid data collection, DECHEMA (1977). The books by Chu *et al.* (1956), Hala *et al.* (1968, 1973), Hirata *et al.* (1975) and Ohe (1989, 1990) are also useful sources.

### 8.16.2. Phase equilibria

The criterion for thermodynamic equilibrium between two phases of a multicomponent mixture is that for every component,  $i$ :

$$f_i^v = f_i^L \quad (8.28)$$

where  $f_i^v$  is the vapour-phase fugacity and  $f_i^L$  the liquid-phase fugacity of component  $i$ :

$$f_i^v = \pi \phi_i y_i \quad (8.29)$$

and

$$f_i^L = f_i^{OL} \gamma_i x_i \quad (8.30)$$

where  $\pi$  = total systems pressure

$\phi_i$  = vapour fugacity coefficient

$y_i$  = concentration of component  $i$  in the vapour phase

$f_i^{OL}$  = standard state fugacity of the pure liquid

$\gamma_i$  = liquid-phase activity coefficient

$x_i$  = concentration of component  $i$  in the liquid phase

Substitution from equations 8.29 and 8.30 into equation 8.28, and rearranging gives:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^{OL}}{\pi \phi_i} \quad (8.31)$$

where  $K_i$  is the distribution coefficient (the  $K$  value).

$\phi_i$  can be calculated from an appropriate equation of state (see Section 8.16.3).

$f_i^{OL}$  can be computed from the following expression:

$$f_i^{OL} = P_i^o \phi_i^s \left\{ \exp \left\{ \frac{(\pi - P_i^o)}{RT} v_i^L \right\} \right\} \quad (8.32)$$

where  $P_i^o$  = the pure component vapour pressure (which can be calculated from the Antoine equation, see Section 8.11), N/m<sup>2</sup>

$\phi_i^s$  = the fugacity coefficient of the pure component  $i$  at saturation

$v_i^L$  = the liquid molar volume, m<sup>3</sup>/mol

The exponential term in equation 8.32 is known as the *Poynting* correction, and corrects for the effects of pressure on the liquid-phase fugacity.

$\phi_i^s$  is calculated using the same equation of state used to calculate  $\phi_i$ .

For systems in which the vapour phase imperfections are not significant, equation 8.32 reduces to the familiar Raoult's law equation (see Volume 2, Chapter 11):

$$K_i = \frac{\gamma_i P_i^o}{\pi} \quad (8.33)$$

### **Relative volatility**

The relative volatility of two components can be expressed as the ratio of their  $K$  values:

$$\alpha_{ij} = \frac{K_i}{K_j} \quad (8.34)$$

For ideal mixtures (obeying Raoult's law):

$$K_i = \frac{P_i^o}{P} \quad (8.35)$$

and

$$\alpha_{ij} = \frac{K_i^o}{K_j^o} = \frac{P_i^o}{P_j^o} \quad (8.36)$$

where  $K_i^o$  and  $K_j^o$  are the ideal  $K$  values for components  $i$  and  $j$ .

### 8.16.3. Equations of state

An equation of state is an algebraic expression which relates temperature, pressure and molar volume, for a real fluid.

Many equations of state have been developed, of varying complexity. No one equation is sufficiently accurate to represent all real gases, under all conditions. The equations of state most frequently used in the design of multicomponent separation processes are given below. The actual equation is only given for one of the correlations, the Redlich–Kwong equation, as an illustration. Equations of state would normally be incorporated in computer aided design packages; see Chapter 11. For details of the other equations the reader should consult the reference cited, or the books by Reid *et al.* (1987) and Walas (1989). To selection the best equation to use for a particular process design refer to Table 8.11 and Figure 8.4.

#### **Redlich–Kwong equation (R–K)**

This equation is an extension of the more familiar *Van der Waal's* equation. The *Redlich–Kwong* equation is:

$$P = \frac{PT}{V - b} \times \frac{a}{T^{1/2}V(V + b)} \quad (8.37)$$

where  $a = 0.427 \mathbf{R}^2 T_c^{2.5} / P_c$

$b = 0.08664 \mathbf{R} T_c / P_c$

$P$  = pressure

$V$  = volume

The R–K equation is not suitable for use near the critical pressure ( $P_r > 0.8$ ), or for liquids; Redlich and Kwong (1949).

#### **Redlich–Kwong–Soave equation (R–K–S)**

Soave (1972) modified the *Redlich–Kwong* equation to extend its usefulness to the critical region, and for use with liquids.

#### **Benedict–Webb–Rubin (B–W–R) equation**

This equation has eight empirical constants and gives accurate predictions for vapour and liquid phase hydrocarbons. It can also be used for mixtures of light hydrocarbons with carbon dioxide and water; Benedict *et al.* (1951).

#### **Lee–Kesler–Plocker (L–K–P) equation**

Lee and Kesler (1975) extended the *Benedict–Webb–Rubin* equation to a wider variety of substances, using the principle of corresponding states. The method was modified further by Plocker *et al.* (1978).

### **Chao–Seader equation (C–S)**

The *Chao–Seader* equation gives accurate predictions for light hydrocarbons and hydrogen, but is limited to temperatures below 530 K; Chao and Seader (1961).

### **Grayson–Stread equation (G–S)**

Grayson and Stread (1963) extended the *Chao–Seader* equation for use with hydrogen rich mixtures, and for high pressure and high temperature systems. It can be used up to 200 bar and 4700 K.

### **Peng–Robinson equation (P–R)**

The Peng–Robinson equation is related to the *Redlich–Kwong–Soave* equation of state and was developed to overcome the instability in the *Redlich–Kwong–Soave* equation near the critical point; Peng and Robinson (1970).

### **Brown $K_{10}$ equation (B–K10)**

Brown, see Cajander *et al.* (1960), developed a method which relates the equilibrium constant  $K$  to four parameters: component, pressure, temperature, and the convergence pressure. The convergence pressure is the pressure at which all  $K$  values tend to 1. The *Brown  $K_{10}$*  equation is limited to low pressure and its use is generally restricted to vacuum systems.

## **8.16.4. Correlations for liquid phase activity coefficients**

The liquid phase activity coefficient,  $\gamma_i$ , is a function of pressure, temperature and liquid composition. At conditions remote from the critical conditions it is virtually independent of pressure and, in the range of temperature normally encountered in distillation, can be taken as independent of temperature.

Several equations have been developed to represent the dependence of activity coefficients on liquid composition. Only those of most use in the design of separation processes will be given. For a detailed discussion of the equations for activity coefficients and their relative merits the reader is referred to the book by Reid *et al.* (1987), Walas (1984) and Null (1970).

### **Wilson equation**

The equation developed by Wilson (1964) is convenient to use in process design:

$$\ln \gamma_k = 1.0 - \ln \left[ \sum_{j=1}^n (x_j A_{kj}) \right] - \sum_{i=1}^n \left[ \frac{x_i A_{ik}}{\sum_{j=1}^n (x_j A_{ij})} \right] \quad (8.38)$$

where  $\gamma_k$  = activity coefficient for component  $k$ ,

$A_{ij}, A_{ji}$  = Wilson coefficients ( $A$  values) for the binary pair  $i, j$ ,

$n$  = number of components.

The Wilson equation is superior to the familiar Van-Laar and Margules equations (see Volume 2, Chapter 11) for systems that are severely non-ideal; but, like other three suffix equations, it cannot be used to represent systems that form two phases in the concentration range of interest.

A significant advantage of the Wilson equation is that it can be used to calculate the equilibrium compositions for multicomponent systems using only the Wilson coefficients obtained for the binary pairs that comprise the multicomponent mixture. The Wilson coefficients for several hundred binary systems are given in the DECHEMA vapour-liquid data collection, DECHEMA (1977), and by Hirata (1975). Hirata gives methods for calculating the Wilson coefficients from vapour liquid equilibrium experimental data.

The Wilson equation is best solved using a short computer program with the Wilson coefficients in matrix form, or by using a spreadsheet. A suitable program is given in Table 8.9 and its use illustrated in Example 8.9. The program language is GWBASIC and it is intended for interactive use. It can be extended for use with any number of components by changing the value of the constant  $N$  in the first data statement and including the

Table 8.9. Program for Wilson equation (Example 8.15)

---

```

100 REM WILSON EQUATION
110 REM CALCULATES ACTIVITY COEFFICIENTS FOR MULTICOMPONENT SYSTEMS
120 PRINT ``DATA STATEMENTS LINES 410 TO 450``
130 READ N
140 REM MAT READ A
150 FOR I = 1 TO N
160 FOR J = 1 TO N
170 READ A(I, J)
180 NEXT J
190 NEXT I
200 PRINT ``TYPE IN LIQUID COMPOSITION, ONE COMPONENT AT A TIME``
210 FOR P=1 TO N
220 PRINT ``X``;P;``?``
230 INPUT X(P)
240 NEXT P
250 FOR K=1 TO N
260 Q1=0
270 FOR J=1 TO N
280 Q1=Q1+X(J)*A(K,J)
290 NEXT J
300 Q2=0
310 FOR I=1 TO N
320 Q3=0
330 FOR J=1 TO N
340 Q3=Q3+X(J)*A(I,J)
350 NEXT J
360 Q2=Q2+(X(I)*A(I,K))/Q3
370 NEXT I
380 G(K) = EXP(1-LOG(Q1)-Q2)
390 PRINT ``GAMMA``;K;``=``;G(K)
400 NEXT K
410 DATA 4
420 DATA 1,2.3357,2.7385,0.4180
430 DATA 0.1924,1,1.6500,0.1108
440 DATA 0.2419,0.5343,1,0.0465
450 DATA 0.9699,0.9560,0.7795,1
460 END

```

---



appropriate Wilson coefficients (Wilson  $A$  values) in the other data statements. The program can easily be modified for use as a sub-routine for bubble-point and other vapour composition programs.

The use of a spreadsheet to solve the Wilson equation is illustrated in Example 8.15*b*. The spreadsheet used was Microsoft Excel. Copies of the spreadsheet example can be downloaded from support material for this chapter given on the publisher's web site at: [bh.com/companions/075641428](http://bh.com/companions/075641428).

### Example 8.15*a*

Using the Wilson equation, calculate the activity coefficients for isopropyl alcohol (IPA) and water in a mixture of IPA, methanol, water, and ethanol; composition, all mol fraction:

Methanol	Ethanol	IPA	Water
0.05	0.05	0.18	0.72

### Solution

Use the binary Wilson  $A$  values given by Hirata (1975). The program "WILSON", Table 8.9, is used to solve this example.

The Wilson  $A$ -values for the binary pairs are  $A_{i,j}$

		$j$			
		1	2	3	4
$i$	[	1	2.3357	2.7385	0.4180
		0.1924	1	1.6500	0.1108
		0.2419	0.5343	1	0.0465
		0.9699	0.9560	0.7795	1
	]				

Component 1 = MeOH

2 = EtOH

3 = IPA

4 = H<sub>2</sub>O

The output from the program for the concentrations given was:

$$\gamma_3 = 2.11, \quad \gamma_4 = 1.25$$

Experimental values from Hirata (1975)

$$\gamma_3 = 2.1, \quad \gamma_4 = 1.3$$

### Example 8.15*b*

Using the compositions and Wilson coefficients given in Example 8.15*a*, determine the activity coefficient for methanol.

**Solution****Matrix of coefficients**

		j			
		1	2	3	4
i	1	1	2.3357	2.7385	0.4180
	2	0.1924	1	1.6500	0.1108
	3	0.2419	0.5343	1	0.0465
	4	0.9699	0.956	0.7795	1

		k			
		1	2	3	4
comp	MeOH	0.05	0.05	0.18	0.72
	EtOH	0.05	0.05	0.18	0.72
	IPA	0.05	0.05	0.18	0.72
	H2O	0.05	0.05	0.18	0.72

$$Q1 = x(j) * A(k, j)$$

k = 1		
j = 1	Q1 =	0.05
j = 2		0.116785
j = 3		0.4929
j = 4		0.30096
sumQ1		0.960675

$$Q3 = x(j) * A(i, j)$$

		i = 1	i = 2	i = 3	i = 4
j = 1	Q3 =	0.05	0.00962	0.012095	0.048495
j = 2		0.116785	0.05	0.026715	0.0478
j = 3		0.49293	0.297	0.18	0.14031
j = 4		0.30096	0.079776	0.03348	0.72
sum		0.960675	0.436396	0.25229	0.956605

$$Q2 = x(i) * A(i, k) / \text{sum}Q3$$

	Q2 =	k = 1
i = 1		0.052047
i = 2		0.022044
i = 3		0.172587
i = 4		0.730007
sum		0.976685

$$\text{Gamma } k = \exp(1 - \ln(\text{sum}Q1) - \text{sum}Q2)$$

$$\text{gamma } 1 = \underline{\underline{1.06549}}$$

**Non-random two liquid equation (NRTL) equation**

The NRTL equation developed by Renon and Prausnitz overcomes the disadvantage of the Wilson equation in that it is applicable to immiscible systems. If it can be used to predict phase compositions for vapour-liquid and liquid-liquid systems.

### **Universal quasi-chemical (UNIQUAC) equation**

The UNIQUAC equation developed by Abrams and Prausnitz is usually preferred to the NRTL equation in the computer aided design of separation processes. It is suitable for miscible and immiscible systems, and so can be used for vapour-liquid and liquid-liquid systems. As with the Wilson and NRTL equations, the equilibrium compositions for a multicomponent mixture can be predicted from experimental data for the binary pairs that comprise the mixture. Also, in the absence of experimental data for the binary pairs, the coefficients for use in the UNIQUAC equation can be predicted by a group contribution method: UNIFAC, described below.

The UNIQUAC equation is not given here as its algebraic complexity precludes its use in manual calculations. It would normally be used as a sub-routine in a design or process simulation program. For details of the equation consult the texts by Reid *et al.* (1987) or Walas (1984).

The best source of data for the UNIQUAC constants for binary pairs is the DECHEMA vapour-liquid and liquid-liquid data collection, DECHEMA (1977).

### **8.16.5. Prediction of vapour-liquid equilibria**

The designer will often be confronted with the problem of how to proceed with the design of a separation process without adequate experimentally determined equilibrium data. Some techniques are available for the prediction of vapour-liquid equilibria (v-l-e) data and for the extrapolation of experimental values. Caution must be used in the application of these techniques in design and the predictions should be supported with experimentally determined values whenever practicable. The same confidence cannot be placed on the prediction of equilibrium data as that for many of the prediction techniques for other physical properties given in this chapter. Some of the techniques most useful in design are given in the following paragraphs.

#### **Estimation of activity coefficients from azeotropic data**

If a binary system forms an azeotrope, the activity coefficients can be calculated from a knowledge of the composition of the azeotrope and the azeotropic temperature. At the azeotropic point the composition of the liquid and vapour are the same, so from equation 8.31:

$$\gamma_i = \frac{P}{P_i^\circ}$$

where  $P_i^\circ$  is determined at the azeotropic temperature.

The values of the activity coefficients determined at the azeotropic composition can be used to calculate the coefficients in the Wilson equation (or any other of the three-suffix equations) and the equation used to estimate the activity coefficients at other compositions.

Horsley (1973) gives an extensive collection of data on azeotropes.

### **Activity coefficients at infinite dilution**

The constants in any of the activity coefficient equations can be readily calculated from experimental values of the activity coefficients at infinite dilution. For the Wilson equation:

$$\ln \gamma_1^\infty = -\ln A_{12} - A_{21} + 1 \quad (8.39a)$$

$$\ln \gamma_2^\infty = -\ln A_{21} - A_{12} + 1 \quad (8.39b)$$

where  $\gamma_1^\infty, \gamma_2^\infty$  = the activity coefficients at infinite dilution for components 1 and 2, respectively,

$A_{12}$  = the Wilson A-value for component 1 in component 2,

$A_{21}$  = the Wilson A-value for component 2 in component 1.

Relatively simple experimental techniques, using ebulliometry and chromatography, are available for the determination of the activity coefficients at infinite dilution. The methods used are described by Null (1970) and Conder and Young (1979).

Pieratti *et al.* (1955) have developed correlations for the prediction of the activity coefficients at infinite dilution for systems containing water, hydrocarbons and some other organic compounds. Their method, and the data needed for predictions, is described by Treybal (1963) and Reid *et al.* (1987).

### **Calculation of activity coefficients from mutual solubility data**

For systems that are only partially miscible in the liquid state, the activity coefficient in the homogeneous region can be calculated from experimental values of the mutual solubility limits. The methods used are described by Reid *et al.* (1987), Treybal (1963), Brian (1965) and Null (1970). Treybal (1963) has shown that the Van-Laar equation should be used for predicting activity coefficients from mutual solubility limits.

### **Group contribution methods**

Group contribution methods have been developed for the prediction of liquid-phase activity coefficients. The objective has been to enable the prediction of phase equilibrium data for the tens of thousands of possible mixtures of interest to the process designer to be made from the contributions of the relatively few functional groups which made up the compounds. The UNIFAC method, Fredenslund *et al.* (1977a), is probably the most useful for process design. Its use is described in detail in a book by Fredenslund *et al.* (1977b), which includes computer programs and data for the use of the UNIFAC method in the design of distillation columns.

A method was also developed to predict the parameters required for the NRTL equation: the ASOG method, Kojima and Tochigi (1979).

More extensive work has been done to develop the UNIFAC method, to include a wider range of functional groups; see Gmeling *et al.* (1982) and Magnussen *et al.* (1981).

The UNIFAC equation is the preferred equation for use in design, and it is included as a sub-routine in most simulation and design programs.

Care must be exercised in applying the UNIFAC method. The specific limitations of the method are:

1. Pressure not greater than a few bar (say, limit to 5 bar)
2. Temperature below 150°C
3. No non-condensable components or electrolytes
4. Components must not contain more than 10 functional groups.

#### **8.16.6. *K*-values for hydrocarbons**

A useful source of *K*-values for light hydrocarbons is the well-known “De Priester charts”, Dabyburjor (1978), which are reproduced as Figure 8.3*a* and *b*. These charts give the *K*-values over a wide range of temperature and pressure.

#### **8.16.7. Sour-water systems (Sour)**

The term *sour water* is used for water containing carbon dioxide, hydrogen sulphide and ammonia encountered in refinery operations.

Special correlations have been developed to handle the vapour-liquid equilibria of such systems, and these are incorporated in most design and simulation programs.

Newman (1991) gives the equilibrium data required for the design of sour water systems, as charts.

#### **8.16.8. Vapour-liquid equilibria at high pressures**

At pressures above a few atmospheres, the deviations from ideal behaviour in the gas phase will be significant and must be taken into account in process design. The effect of pressure on the liquid-phase activity coefficient must also be considered. A discussion of the methods used to correlate and estimate vapour-liquid equilibrium data at high pressures is beyond the scope of this book. The reader should refer to the texts by Null (1970) or Prausnitz and Chueh (1968).

Prausnitz and Chueh also discuss phase equilibria in systems containing components above their critical temperature (super-critical components).

#### **8.16.9. Liquid-liquid equilibria**

Experimental data, or predictions, that give the distribution of components between the two solvent phases, are needed for the design of liquid-liquid extraction processes; and mutual solubility limits will be needed for the design of decanters, and other liquid-liquid separators.

Perry *et al.* (1997) give a useful summary of solubility data. Liquid-liquid equilibrium compositions can be predicted from vapour-liquid equilibrium data, but the predictions are seldom accurate enough for use in the design of liquid-liquid extraction processes.

Null (1970) gives a computer program for the calculation of ternary diagrams from vle data, using the Van-Laar equation.

The DECHEMA data collection includes liquid-liquid equilibrium data for several hundred mixtures, DECHEMA (1977).

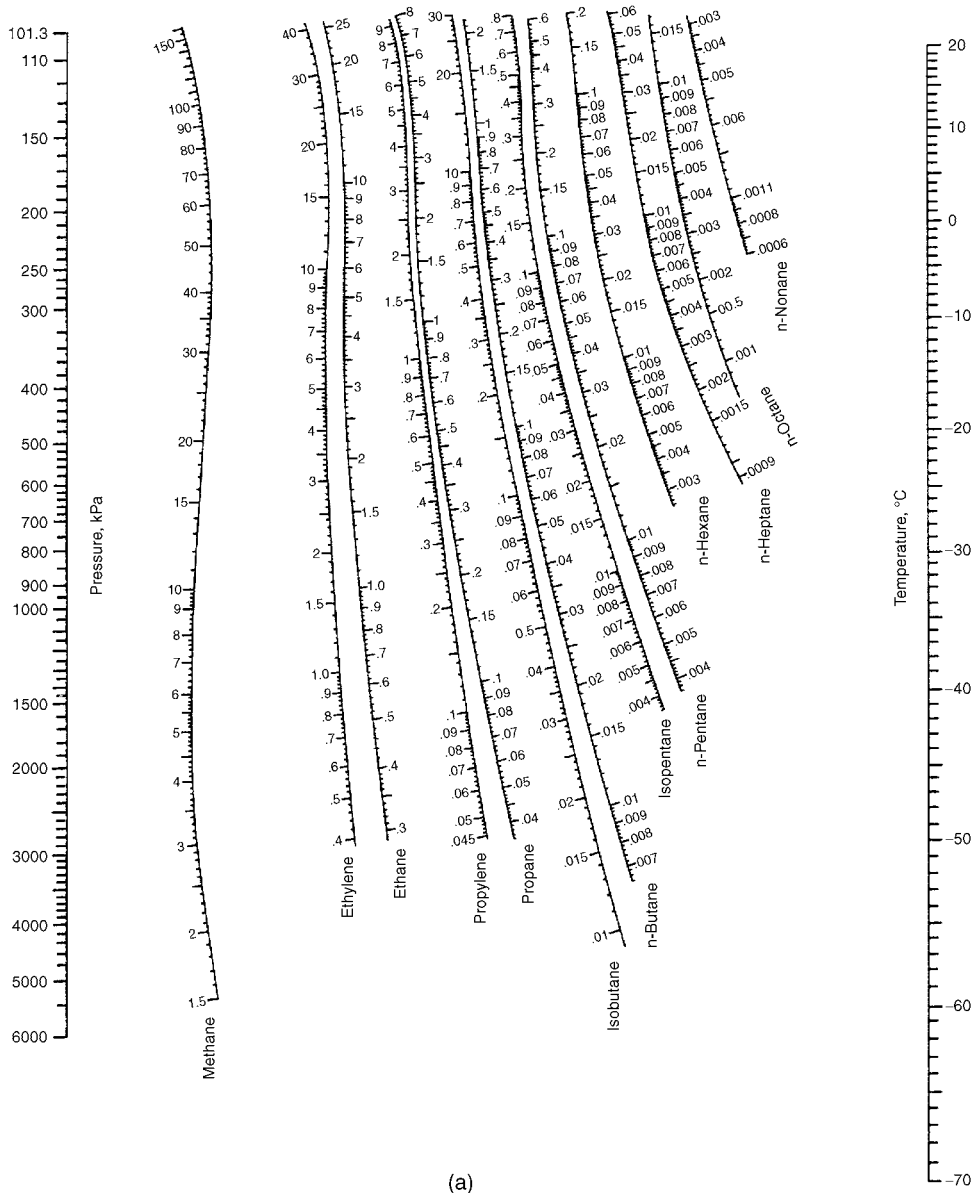


Figure 8.3. (a) De Priester chart— $K$ -values for hydrocarbons, low temperature

The UNIQUAC equation can be used to estimate activity coefficients and liquid compositions for multicomponent liquid-liquid systems. The UNIFAC method can be used to estimate UNIQUAC parameters when experimental data are not available, see Section 8.16.5.

It must be emphasised that extreme caution needs to be exercised when using predicted values for liquid activity coefficients in design calculations.

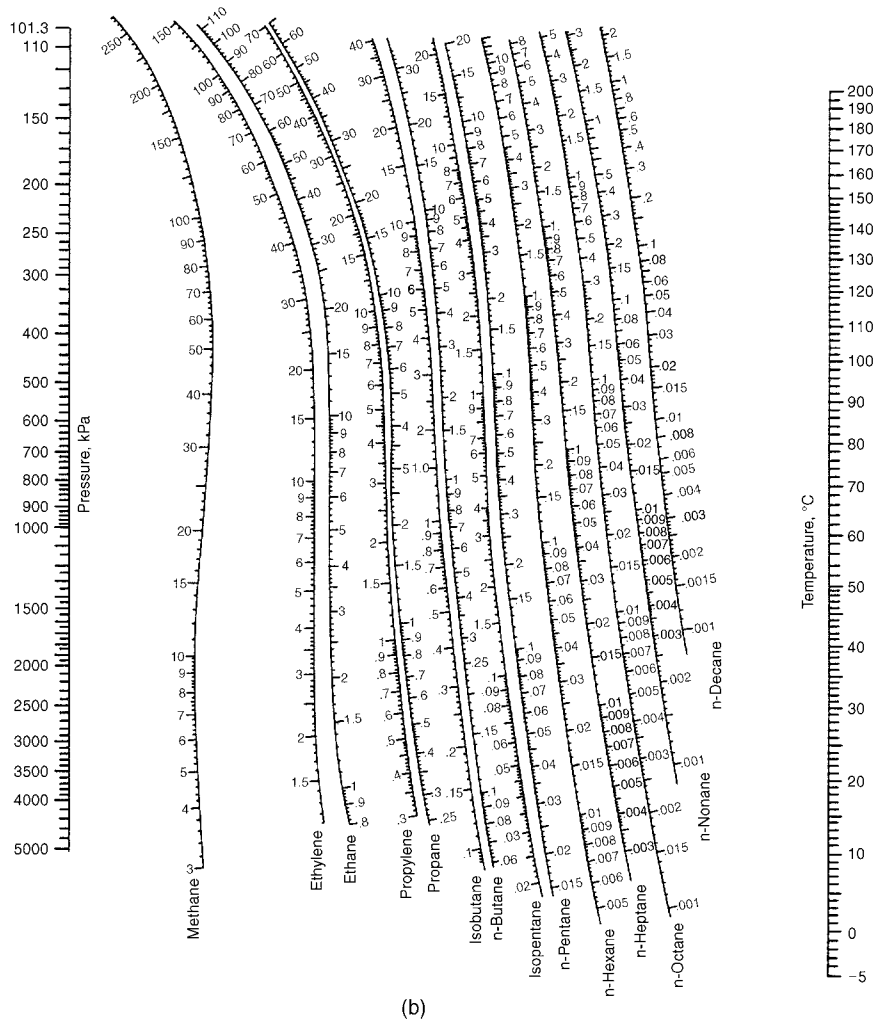


Figure 8.3. (b) De Priester chart— $K$ -values for hydrocarbons, high temperature

### 8.16.10. Choice of phase equilibria for design calculations

The choice of the best method for deducing vapour-liquid and liquid-liquid equilibria for a given system will depend on three factors:

1. The composition of the mixture (the class of system)
2. The operating pressure (low, medium or high)
3. The experimental data available.

#### **Classes of mixtures**

For the purpose of deciding which phase equilibrium method to use, it is convenient to classify components into the classes shown in Table 8.10.

Table 8.10. Classification of mixtures

	Class	Principal interactions	Examples
I.	Simple molecules	Dispersion forces	H <sub>2</sub> , N <sub>2</sub> , CH <sub>4</sub>
II.	Complex non-polar molecules	Dispersion forces	CCl <sub>4</sub> , iC <sub>5</sub> H <sub>10</sub>
III.	Polarisable	Induction dipole	CO <sub>2</sub> , C <sub>6</sub> H <sub>6</sub>
IV.	Polar molecules	Dipole moment	dimethyl formamide, chloroethane
V.	Hydrogen bonding	Hydrogen bonds	alcohols, water

Table 8.11. Selection of phase equilibrium method

Class of mixture	Low <3 bar		Pressure Moderate <15 bar		High >15 bar	
	$f^L$	$f^V$	$f^L$	$f^V$	$f^L$	$f^V$
I, II, III (none supercritical)	ES	I	ES	ES	ES	ES and K
I, II, III (supercritical)	ES	I	ES	ES	ES	ES and K
I, II, III, IV, V (vapour-liquid)	ACT	I	ACT	ES	ES	ES and K
I, II, III, IV, V (liquid-liquid)	ACT	I	ACT	ES	ES	ES
Hydrocarbons and water	ES	ES and K	ES	ES and K	ES	ES and K

I = Ideal, vapour fugacity = partial pressure.

ES = appropriate equation of state.

K = equilibrium constant (K factor) derived from experimental data.

ACT = correlation for liquid-phase activity coefficient: such as, Wilson, NRTL, UNIQUAC, UNIFAC. (See Section 8.16.4). Use UNIQUAC and UNIFAC v-1-e parameters for vapour-liquid systems and l-l-e parameters for liquid-liquid systems.

Using the classification given in Table 8.10, Table 8.11 can be used to select the appropriate vapour-liquid and liquid-liquid phase equilibria method.

### **Flow chart for selection of phase equilibria method**

The flow chart shown in Figure 8.4 has been adapted from a similar chart published by Wilcon and White (1986). The abbreviations used in the chart for the equations of state correspond to those given in Section 8.16.3.

#### **8.16.11. Gas solubilities**

At low pressures, most gases are only sparingly soluble in liquids, and at dilute concentrations the systems obey Henry's law (see Volume 2, Chapter 11). Markham and Kobe (1941) and Battino and Clever (1966) give comprehensive reviews of the literature on gas solubilities.



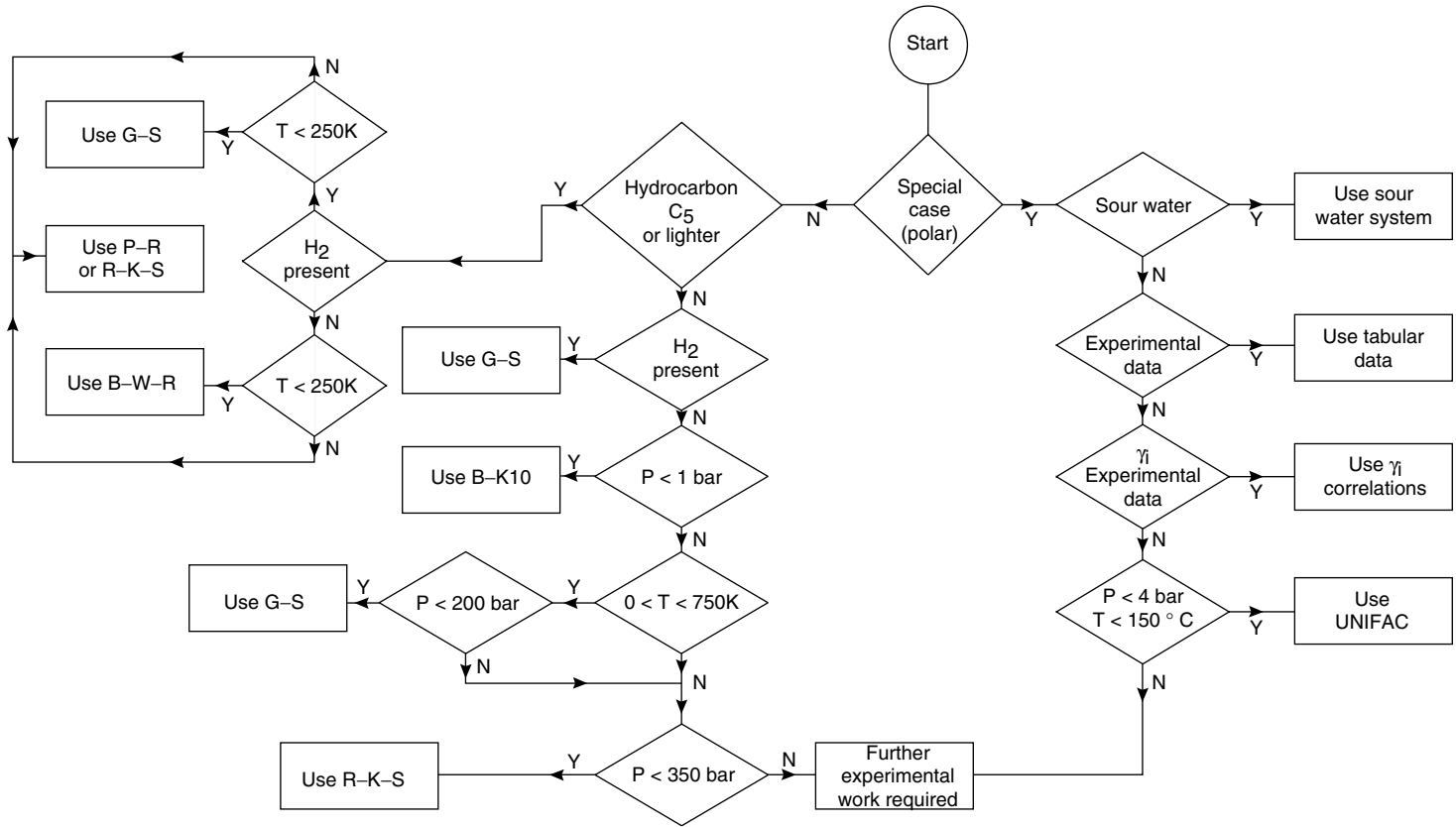


Figure 8.4. Flow chart for the selection of phase equilibria method

### 8.16.12. Use of equations of state to estimate specific enthalpy and density

Computer aided packages for the design and simulation of separation processes will contain sub-routines for the estimation of excess enthalpy and liquid and vapour density from the appropriate equation of state.

#### **Specific enthalpy**

For the vapour phase, the deviation of the specific enthalpy from the ideal state can be illustrated using the *Redlich-Kwong* equation, written in the form:

$$z^3 + z^2 + z(B^2 + B - A) = 0$$

where  $z$  = the compressibility factor

$$A = \frac{a \times P}{R^2 \times T^{2.5}}$$

$$B = \frac{b \times P}{R \times T}$$

The fugacity coefficient is given by:

$$\ln \phi = z - 1 - \ln(z - b) - \left(\frac{A}{B}\right) \ln \left(1 - \frac{B}{z}\right)$$

$$\text{and the excess enthalpy } (H - H^\circ) = RT + \int_0^v \left[ T \left( \frac{dP}{dT} \right)_v - P \right] dv$$

where  $H$  is enthalpy at the system temperature and pressure and  $H^\circ$  enthalpy at the ideal state.

Unless liquid phase activity coefficients have been used, it is best to use the same equation of state for excess enthalpy that was selected for the vapour-liquid equilibria. If liquid-phase activity coefficients have been specified, then a correlation appropriate for the activity coefficient method should be used.

#### **Density**

For vapours, use the equation of state selected for predicting the vapour-liquid equilibria. For liquids, use the same equation if it is suitable for estimating liquid density.

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## 8.18. NOMENCLATURE

	Dimensions in $MLT\theta$
$A$	—
$A_{1,2}$	—
$a$	—
$B$	$\theta$
$B_i$	$M^{-1}L^3$
$b$	—
$C$	$\theta$
$C_p$	$L^2T^{-2}\theta^{-1}$
$D_L$	$L^2T^{-1}$
$D_v$	$L^2T^{-1}$
$f_i$	—
$f_i^{OL}$	—
$H$	$L^2T^{-2}$
$H^0$	$L^2T^{-2}$
$I$	$M^{-1}L^3$
$K$	—
$K^0$	—
$k$	$MLT^{-3}\theta^{-1}$
$k_m$	$MLT^{-3}\theta^{-1}$
$L_v$	$L^2T^{-2}$
$L_{v,b}$	$L^2T^{-2}$
$M$	$M$
$n$	—
$P$	$ML^{-1}T^{-2}$ or $L$
$P_c$	$ML^{-1}T^{-2}$
$P_{ch}$	—
$P_i^0$	$ML^{-1}T^{-2}$ or $L$
$P_k$	$ML^{-1}T^{-2}$ or $L$
$P_r$	—
$\Delta P_c$	$M^{-1/2}L^{1/2}T$
$R$	$L^2T^{-2}\theta^{-1}$
$T$	$\theta$
$T_b$	$\theta$
$T_c$	$\theta$
$T_r$	—
$\Delta T_c$	—
$t$	$\theta$
$V_c$	$M^{-1}L^3$
$V_m$	$M^{-1}L^3$
$\Delta V_c$	$M^{-1}L^3$
$v_i$	$L^3$
$v_i^0$	$M^{-1}L^3$
$w$	—
$x$	—
$y$	—
$z$	—

$\alpha$	Relative volatility	—
$\beta$	Coefficient of thermal expansion	$\theta^{-1}$
$\gamma$	Liquid activity coefficient	—
$\gamma^\infty$	Activity coefficient at infinite dilution	—
$\mu$	Dynamic viscosity	$ML^{-1}T^{-1}$
$\mu_b$	Viscosity at boiling point	$ML^{-1}T^{-1}$
$\mu_m$	Viscosity of a mixture	$ML^{-1}T^{-1}$
$\rho$	Density	$ML^{-3}$
$\rho_L$	Liquid density	$ML^{-3}$
$\rho_v$	Vapour (gas) density	$ML^{-3}$
$\rho_b$	Density at normal boiling point	$ML^{-3}$
$\sigma$	Surface tension	$MT^{-2}$
$\sigma_m$	Surface tension of a mixture	$MT^{-2}$
$\phi$	Fugacity coefficient	—
$\phi^s$	Fugacity coefficient of pure component	—
$\phi^L$	Fugacity coefficient of pure liquid	—
$\phi^V$	Fugacity coefficient of pure vapour	—
Suffixes		
$a, b$	} Components	
$i, j, k$		
$1, 2$		
L	Liquid	—
v	Vapour	—

## 8.19. PROBLEMS

**8.1.** Estimate the liquid density at their boiling points for the following:

1. 2-butanol,
2. Methyl chloride,
3. Methyl ethyl ketone,
4. Aniline,
5. Nitrobenzene.

**8.2.** Estimate the density of the following gases at the conditions given:

1. Hydrogen at 20 bara and 230 °C,
2. Ammonia at 1 bara and 50 °C and at 100 bara and 300 °C,
3. Nitrobenzene at 20 bara and 230 °C,
4. Water at 100 bara and 500 °C. Check your answer using steam tables,
5. Benzene at 2 barg and 250 °C,
6. Synthesis gas ( $N_2 + 3H_2$ ) at 5 barg and 25 °C.

**8.3.** Make a rough estimate of the viscosity of 2-butanol and aniline at their boiling points, using the modified Arrhenius equation. Compare your values with those given using the equation for viscosity in Appendix C.

**8.4.** Make a rough estimate of the thermal conductivity of n-butane both as a liquid at 20 °C and as a gas at 5 bara and 200 °C. Take the viscosity of the gaseous n-butane as 0.012 mN m<sup>-2</sup>s.

**8.5.** Estimate the specific heat capacity of liquid 1,4 pentadiene and aniline at 20 °C.

- 8.6.** For the compounds listed below, estimate the constants in the equation for ideal gas heat capacity, equation 3.19, using the method given in Section 8.9.2.
1. 3-methyl thiophene.
  2. Nitrobenzene.
  3. 2-methyl-2-butanethiol.
  4. Methyl-t-butyl ether.
- 8.7.** Estimate the heat of vaporisation of methyl-t-butyl ether, at 100 °C.
- 8.8.** Estimate the gaseous phase diffusion coefficient for the following systems, at 1 atmosphere and the temperatures given:
1. Carbon dioxide in air at 20 °C,
  2. Ethane in hydrogen at 0 °C,
  3. Oxygen in hydrogen at 0 °C,
  4. Water vapour in air at 450 °C,
  5. Phosgene in air at 0 °C.
- 8.9.** Estimate the liquid phase diffusion coefficient for the following systems at 25 °C:
1. Toluene in n-heptane,
  2. Nitrobenzene in carbon tetrachloride,
  3. Chloroform in benzene,
  4. Hydrogen chloride in water,
  5. Sulphur dioxide in water.
- 8.10.** Estimate the surface tension of pure acetone and ethanol at 20 °C, and benzene at 16 °C, all at 1 atmosphere pressure.
- 8.11.** Using Lydersen's method, estimate the critical constants for isobutanol. Compare your values with those given in Appendix C.
- 8.12.** The composition of the feed to a debutaniser is given below. The column will operate at 14 bar and below 750 K. The process is to be modelled using a commercial simulation program. Suggest a suitable phase equilibrium method to use in the simulation.
- Feed composition:

		kg/h
propane	C <sub>3</sub>	910
isobutane	i-C <sub>4</sub>	180
n-butane	n-C <sub>4</sub>	270
isopentane	i-C <sub>5</sub>	70
normal pentane	n-C <sub>5</sub>	90
normal hexane	n-C <sub>6</sub>	20

- 8.13.** In the manufacture of methyl ethyl ketone from butanol, the product is separated from unreacted butanol by distillation. The feed to the column consists of a mixture of methyl ethyl ketone, 2-butanol and trichloroethane. What would be a suitable phase equilibrium correlation to use in modelling this process?



## *Safety and Loss Prevention*

### 9.1. INTRODUCTION

Any organisation has a legal and moral obligation to safeguard the health and welfare of its employees and the general public. Safety is also good business; the good management practices needed to ensure safe operation will also ensure efficient operation.

The term “loss prevention” is an insurance term, the loss being the financial loss caused by an accident. This loss will not only be the cost of replacing damaged plant and third party claims, but also the loss of earnings from lost production and lost sales opportunity.

All manufacturing processes are to some extent hazardous, but in chemical processes there are additional, special, hazards associated with the chemicals used and the process conditions. The designer must be aware of these hazards, and ensure, through the application of sound engineering practice, that the risks are reduced to acceptable levels.

In this book only the particular hazards associated with chemical and allied processes will be considered. The more general, normal, hazards present in all manufacturing process such as, the dangers from rotating machinery, falls, falling objects, use of machine tools, and of electrocution will not be considered. General industrial safety and hygiene are covered in several books, King and Hirst (1998), Ashafi (2003) and Ridley (2003).

Safety and loss prevention in process design can be considered under the following broad headings:

1. Identification and assessment of the hazards.
2. Control of the hazards: for example, by containment of flammable and toxic materials.
3. Control of the process. Prevention of hazardous deviations in process variables (pressure, temperature, flow), by provision of automatic control systems, interlocks, alarms, trips; together with good operating practices and management.
4. Limitation of the loss. The damage and injury caused if an incident occurs: pressure relief, plant layout, provision of fire-fighting equipment.

In this chapter the discussion of safety in process design will of necessity be limited. A more complete treatment of the subject can be found in the books by Wells (1980) (1997), Lees (1996), Fawcett and Wood (1984), Green (1982) and Carson and Mumford (1988) (2002); and in the general literature, particularly the publications by the American Institute of Chemical Engineers and the Institution of Chemical Engineers. The proceedings of the symposia on safety and loss prevention organised by these bodies, and the European Federation of Chemical Engineering, also contain many articles of interest on general safety philosophy, techniques and organisation, and the hazards associated with specific

processes and equipment. The Institution of Chemical Engineers has published a book on safety of particular interest to students of Chemical Engineering, Marshall and Ruhemann (2000).

## 9.2. INTRINSIC AND EXTRINSIC SAFETY

Processes can be divided into those that are intrinsically safe, and those for which the safety has to be engineered in. An intrinsically safe process is one in which safe operation is inherent in the nature of the process; a process which causes no danger, or negligible danger, under all foreseeable circumstances (all possible deviations from the design operating conditions). The term inherently safe is often preferred to intrinsically safe, to avoid confusion with the narrower use of the term intrinsically safe as applied to electrical equipment (see Section 9.3.4).

Clearly, the designer should always select a process that is inherently safe whenever it is practical, and economic, to do so. However, most chemical manufacturing processes are, to a greater or lesser extent, inherently unsafe, and dangerous situations can develop if the process conditions deviate from the design values.

The safe operation of such processes depends on the design and provision of engineered safety devices, and on good operating practices, to prevent a dangerous situation developing, and to minimise the consequences of any incident that arises from the failure of these safeguards.

The term “engineered safety” covers the provision in the design of control systems, alarms, trips, pressure-relief devices, automatic shut-down systems, duplication of key equipment services; and fire-fighting equipment, sprinkler systems and blast walls, to contain any fire or explosion.

The design of inherently safe process plant is discussed by Kletz in a booklet published by the Institution of Chemical Engineers, Kletz (1984) and Kletz and Cheaper (1998). He makes the telling point that what you do not have cannot leak out: so cannot catch fire, explode or poison anyone. Which is a plea to keep the inventory of dangerous material to the absolute minimum required for the operation of the process.

## 9.3. THE HAZARDS

In this section the special hazards of chemicals are reviewed (toxicity, flammability and corrosivity); together with the other hazards of chemical plant operation.

### 9.3.1. Toxicity

Most of the materials used in the manufacture of chemicals are poisonous, to some extent. The potential hazard will depend on the inherent toxicity of the material and the frequency and duration of any exposure. It is usual to distinguish between the short-term effects (acute) and the long-term effects (chronic). A highly toxic material that causes immediate injury, such as phosgene or chlorine, would be classified as a safety hazard. Whereas a material whose effect was only apparent after long exposure at low concentrations, for instance, carcinogenic materials, such as vinyl chloride, would be classified as industrial

health and hygiene hazards. The permissible limits and the precautions to be taken to ensure the limits are met will be very different for these two classes of toxic materials. Industrial hygiene is as much a matter of good operating practice and control as of good design.

The inherent toxicity of a material is measured by tests on animals. It is usually expressed as the lethal dose at which 50 per cent of the test animals are killed, the LD<sub>50</sub> (lethal dose fifty) value. The dose is expressed as the quantity in milligrams of the toxic substance per kilogram of body weight of the test animal.

Some values for tests on rats are given in Table 9.1. Estimates of the LD<sub>50</sub> for man are based on tests on animals. The LD<sub>50</sub> measures the acute effects; it gives only a crude indication of the possible chronic effects.

Table 9.1. Some LD<sub>50</sub> values

Compound	mg/kg
Potassium cyanide	10
Tetraethyl lead	35
Lead	100
DDT	150
Aspirin	1500
Table salt	3000

Source: Lowrance (1976).

There is no generally accepted definition of what can be considered toxic and non-toxic.

A system of classification is given in the *Classification, Packaging and Labelling of Dangerous Substances, Regulations, 1984* (United Kingdom), which is based on European Union (EU) guidelines; for example:

LD <sub>50</sub> , absorbed orally in rats, mg/kg	
≤25	very toxic
25 to 200	toxic
200 to 2000	harmful

These definitions apply only to the short-term (acute) effects. In fixing permissible limits on concentration for the long-term exposure of workers to toxic materials, the exposure time must be considered together with the inherent toxicity of the material. The “Threshold Limit Value” (TLV) is a commonly used guide for controlling the long-term exposure of workers to contaminated air. The TLV is defined as the concentration to which it is believed the average worker could be exposed to, day by day, for 8 hours a day, 5 days a week, without suffering harm. It is expressed in ppm for vapours and gases, and in mg/m<sup>3</sup> (or grains/ft<sup>3</sup>) for dusts and liquid mists. A comprehensive source of data on the toxicity of industrial materials is Sax’s handbook, Lewis (2004); which also gives guidance on the interpretation and use of the data. Recommended TLV values are published in bulletins by the United States Occupational Safety and Health Administration. Since 1980 the United Kingdom Health and Safety Executive (HSE) has published values for the Occupational Exposure Limits (OEL), for both long and short term exposure, in place of TLV values.

Fuller details of the methods used for toxicity testing, the interpretation of the result and their use in setting standards for industrial hygiene are given in the more specialised texts on the subject; see Carson and Mumford (1988) and Lees (1996).

### ***Control of substances hazardous to health***

In the United Kingdom the use of substances likely to be harmful to employees is covered by regulations issued by the Health and Safety Executive (HSE), under the Health and Safety at Work Act, 1974 (HSAWA). The principal set of regulations in force is the *Control of Substances Hazardous to Health* regulations, 2002; known under the acronym: the *COSHH* regulations. The *COSHH* regulations apply to any hazardous substance in use in any place of work.

The employer is required to carry out an assessment to evaluate the risk to health, and establish what precautions are needed to protect employees. A written record of the assessment would be kept, and details made available to employees.

A thorough explanation of the regulations is not within the scope of this book, as they will apply more to plant operation and maintenance than to process design. The HSE has published a series of booklets giving details of the regulations and their application (see [www.hse.gov.uk/pubns](http://www.hse.gov.uk/pubns)). A comprehensive guide to the *COSHH* regulations has also been published by the Royal Society of Chemistry, Simpson and Simpson (1991).

The designer will be concerned more with the preventative aspects of the use of hazardous substances. Points to consider are:

1. Substitution: of the processing route with one using less hazardous material. Or, substitution of toxic process materials with non-toxic, or less toxic materials.
2. Containment: sound design of equipment and piping, to avoid leaks. For example, specifying welded joints in preference to gasketed flanged joints (liable to leak).
3. Ventilation: use open structures, or provide adequate ventilation systems.
4. Disposal: provision of effective vent stacks to disperse material vented from pressure relief devices; or use vent scrubbers.
5. Emergency equipment: escape routes, rescue equipment, respirators, safety showers, eye baths.

In addition, good plant operating practice would include:

1. Written instruction in the use of the hazardous substances and the risks involved.
2. Adequate training of personnel.
3. Provision of protective clothing.
4. Good housekeeping and personal hygiene.
5. Monitoring of the environment to check exposure levels. Consider the installation of permanent instruments fitted with alarms.
6. Regular medical check-ups on employees, to check for the chronic effects of toxic materials.

### **9.3.2. Flammability**

The term “flammable” is now more commonly used in the technical literature than “inflammable” to describe materials that will burn, and will be used in this book. The hazard caused by a flammable material depends on a number of factors:

1. The flash-point of the material.
2. The autoignition temperature of the material.
3. The flammability limits of the material.
4. The energy released in combustion.

### **Flash-point**

The flash-point is a measure of the ease of ignition of the liquid. It is the lowest temperature at which the material will ignite from an open flame. The flash-point is a function of the vapour pressure and the flammability limits of the material. It is measured in standard apparatus, following standard procedures (BS 2000). Both open- and closed-cup apparatus is used. Closed-cup flash-points are lower than open cup, and the type of apparatus used should be stated clearly when reporting measurements. Flash-points are given in Sax's handbook, Lewis (2004). The flash-points of many volatile materials are below normal ambient temperature; for example, ether  $-45^{\circ}\text{C}$ , petrol (gasoline)  $-43^{\circ}\text{C}$  (open cup).

### **Autoignition temperature**

The autoignition temperature of a substance is the temperature at which it will ignite spontaneously in air, without any external source of ignition. It is an indication of the maximum temperature to which a material can be heated in air; for example, in drying operations.

### **Flammability limits**

The flammability limits of a material are the lowest and highest concentrations in air, at normal pressure and temperature, at which a flame will propagate through the mixture. They show the range of concentration over which the material will burn in air, if ignited. Flammability limits are characteristic of the particular material, and differ widely for different materials. For example, hydrogen has a lower limit of 4.1 and an upper limit of 74.2 per cent by volume, whereas for petrol (gasoline) the range is only from 1.3 to 7.0 per cent.

The Flammability limits for a number of materials are given in Table 9.2.

The limits for a wider range of materials are given in Sax's handbook, Lewis (2004).

A flammable mixture may exist in the space above the liquid surface in a storage tank. The vapour space above highly flammable liquids is usually purged with inert gas (nitrogen) or floating-head tanks are used. In a floating-head tank a "piston" floats on top of the liquid, eliminating the vapour space.

### **Flame traps**

Flame arresters are fitted in the vent lines of equipment that contains flammable material to prevent the propagation of flame through the vents. Various types of proprietary flame arresters are used. In general, they work on the principle of providing a heat sink, usually expanded metal grids or plates, to dissipate the heat of the flame. Flame arrestors and their applications are discussed by Rogowski (1980), Howard (1992) and Mendoza *et al.* (1988).

Traps should also be installed in plant ditches to prevent the spread of flame. These are normally liquid U-legs, which block the spread of flammable liquid along ditches.

Table 9.2. Flammability ranges

Material	Lower limit	Upper limit
Hydrogen	4.1	74.2
Ammonia	15.0	28.0
Hydrocyanic acid	5.6	40.0
Hydrogen sulphide	4.3	45.0
Carbon disulphide	1.3	44.0
Carbon monoxide	12.5	74.2
Methane	5.3	14.0
Ethane	3.0	12.5
Propane	2.3	9.5
Butane	1.9	8.5
Isobutane	1.8	8.4
Ethylene	3.1	32.0
Propylene	2.4	10.3
n-Butene	1.6	9.3
Isobutene	1.8	9.7
Butadiene	2.0	11.5
Benzene	1.4	7.1
Toluene	1.4	6.7
Cyclohexane	1.3	8.0
Methanol	7.3	36.0
Ethanol	4.3	19.0
Isopropanol	2.2	12.0
Formaldehyde	7.0	73.0
Acetaldehyde	4.1	57.0
Aetone	3.0	12.8
Methylethyl ketone	1.8	10.0
Dimethylamine (DEA)	2.8	184
Trimethylamine (TEA)	2.0	11.6
Petrol (gasoline)	1.3	7.0
Paraffin (kerosene)	0.7	5.6
Gas oil (diesel)	6.0	13.5

Volume percentage in air at ambient conditions

### ***Fire precautions***

Recommendations on the fire precautions to be taken in the design of chemical plant are given in the British Standard, BS 5908.

### **9.3.3. Explosions**

An explosion is the sudden, catastrophic, release of energy, causing a pressure wave (blast wave). An explosion can occur without fire, such as the failure through over-pressure of a steam boiler or an air receiver.

When discussing the explosion of a flammable mixture it is necessary to distinguish between detonation and deflagration. If a mixture detonates the reaction zone propagates at supersonic velocity (approximately 300 m/s) and the principal heating mechanism in the mixture is shock compression. In a deflagration the combustion process is the same as in the normal burning of a gas mixture; the combustion zone propagates at subsonic

velocity, and the pressure build-up is slow. Whether detonation or deflagration occurs in a gas-air mixture depends on a number of factors; including the concentration of the mixture and the source of ignition. Unless confined or ignited by a high-intensity source (a detonator) most materials will not detonate. However, the pressure wave (blast wave) caused by a deflagration can still cause considerable damage.

Certain materials, for example, acetylene, can decompose explosively in the absence of oxygen; such materials are particularly hazardous.

### ***Confined vapour cloud explosion (CVCE)***

A relatively small amount of flammable material, a few kilograms, can lead to an explosion when released into the confined space of a building.

### ***Unconfined vapour cloud explosions (UCVCE)***

This type of explosion results from the release of a considerable quantity of flammable gas, or vapour, into the atmosphere, and its subsequent ignition. Such an explosion can cause extensive damage, such as occurred at Flixborough, HMSO (1975). Unconfined vapour explosions are discussed by Munday (1976) and Gugan (1979).

### ***Boiling liquid expanding vapour explosions (BLEVE)***

Boiling liquid expanding vapour explosions occur when there is a sudden release of vapour, containing liquid droplets, due to the failure of a storage vessel exposed to fire. A serious incident involving the failure of a LPG (Liquified Petroleum Gas) storage sphere occurred at Feyzin, France, in 1966, when the tank was heated by an external fire fuelled by a leak from the tank; see Lees (1996) and Marshall (1987).

### ***Dust explosions***

Finely divided combustible solids, if intimately mixed with air, can explode. Several disastrous explosions have occurred in grain silos.

Dust explosions usually occur in two stages: a primary explosion which disturbs deposited dust; followed by the second, severe, explosion of the dust thrown into the atmosphere. Any finely divided combustible solid is a potential explosion hazard. Particular care must be taken in the design of dryers, conveyors, cyclones, and storage hoppers for polymers and other combustible products or intermediates. The extensive literature on the hazard and control of dust explosions should be consulted before designing powder handling systems: Field (1982), Cross and Farrer (1982), Barton (2001), and Eckhoff (2003).

#### **9.3.4. Sources of ignition**

Though precautions are normally taken to eliminate sources of ignition on chemical plants, it is best to work on the principle that a leak of flammable material will ultimately find an ignition source.

### ***Electrical equipment***

The sparking of electrical equipment, such as motors, is a major potential source of ignition, and flame proof equipment is normally specified. Electrically operated instruments, controllers and computer systems are also potential sources of ignition of flammable mixtures.

The use of electrical equipment in hazardous areas is covered by British Standards BS 5345 and BS 5501. The code of practice, BS 5345, Part 1, defines hazardous areas as those where explosive gas-air mixtures are present, or may be expected to be present, in quantities such as to require special precautions for the construction and use of electrical apparatus. Non-hazardous areas are those where explosive gas-air mixtures are not expected to be present.

Three classifications are defined for hazardous areas:

Zone 0: explosive gas-air mixtures are present continuously or present for long periods.  
Specify: intrinsically safe equipment.

Zone 1: explosive gas-air mixtures likely to occur in normal operation.

Specify: intrinsically safe equipment, or flame-proof enclosures: enclosures with pressurizing and purging.

Zone 3: explosive gas-air mixtures not likely to occur during normal operation, but could occur for short periods.

Specify: intrinsically safe equipment, or total enclosure, or non-sparking apparatus.

Consult the standards for the full specification before selecting equipment for use in the designated zones.

The design and specification of intrinsically safe control equipment and systems is discussed by MacMillan (1998) and Cooper and Jones (1993).

### ***Static electricity***

The movement of any non-conducting material, powder, liquid or gas, can generate static electricity, producing sparks. Precautions must be taken to ensure that all piping is properly earthed (grounded) and that electrical continuity is maintained around flanges. Escaping steam, or other vapours and gases, can generate a static charge. Gases escaping from a ruptured vessel can self-ignite from a static spark. For a review of the dangers of static electricity in the process industries, see the article by Napier and Russell (1974); and the books by Pratt (1999) and Britton (1999). A code of practice for the control of static electricity is given in BS 5938 (1991).

### ***Process flames***

Open flames from process furnaces and incinerators are obvious sources of ignition and must be sited well away from plant containing flammable materials.

### ***Miscellaneous sources***

It is the usual practice on plants handling flammable materials to control the entry on to the site of obvious sources of ignition; such as matches, cigarette lighters and battery-operated



equipment. The use of portable electrical equipment, welding, spark-producing tools and the movement of petrol-driven vehicles would also be subject to strict control.

Exhaust gases from diesel engines are also a potential source of ignition.

### 9.3.5. Ionising radiation

The radiation emitted by radioactive materials is harmful to living matter. Small quantities of radioactive isotopes are used in the process industry for various purposes; for example, in level and density-measuring instruments, and for the non-destructive testing of equipment.

The use of radioactive isotopes in industry is covered by government legislation, see [hse.gov.uk/pubns](http://hse.gov.uk/pubns).

A discussion of the particular hazards that arise in the chemical processing of nuclear fuels is outside the scope of this book.

### 9.3.6. Pressure

Over-pressure, a pressure exceeding the system design pressure, is one of the most serious hazards in chemical plant operation. Failure of a vessel, or the associated piping, can precipitate a sequence of events that culminate in a disaster.

Pressure vessels are invariably fitted with some form of pressure-relief device, set at the design pressure, so that (in theory) potential over-pressure is relieved in a controlled manner.

Three basically different types of relief device are commonly used:

*Directly actuated valves:* weight or spring-loaded valves that open at a predetermined pressure, and which normally close after the pressure has been relieved. The system pressure provides the motive power to operate the valve.

*Indirectly actuated valves:* pneumatically or electrically operated valves, which are activated by pressure-sensing instruments.

*Bursting discs:* thin discs of material that are designed and manufactured to fail at a predetermined pressure, giving a full bore opening for flow.

Relief valves are normally used to regulate minor excursions of pressure; and bursting discs as safety devices to relieve major over-pressure. Bursting discs are often used in conjunction with relief valves to protect the valve from corrosive process fluids during normal operation. The design and selection of relief valves is discussed by Morley (1989a,b), and is also covered by the pressure vessel standards, see Chapter 13. Bursting discs are discussed by Mathews (1984), Askquith and Lavery (1990) and Murphy (1993). In the United Kingdom the use of bursting discs is covered by BS 2915. The discs are manufactured in a variety of materials for use in corrosive conditions; such as, impervious carbon, gold and silver; and suitable discs can be found for use with all process fluids.

Bursting discs and relief valves are proprietary items and the vendors should be consulted when selecting suitable types and sizes.

The factors to be considered in the design of relief systems are set out in a comprehensive paper by Parkinson (1979) and by Moore (1984); and in a book published by the Institution of Chemical Engineers, Parry (1992).

## ***Vent piping***

When designing relief venting systems it is important to ensure that flammable or toxic gases are vented to a safe location. This will normally mean venting at a sufficient height to ensure that the gases are dispersed without creating a hazard. For highly toxic materials it may be necessary to provide a scrubber to absorb and “kill” the material; for instance, the provision of caustic scrubbers for chlorine and hydrochloric acid gases. If flammable materials have to be vented at frequent intervals; as, for example, in some refinery operations, flare stacks are used.

The rate at which material can be vented will be determined by the design of the complete venting system: the relief device and the associated piping. The maximum venting rate will be limited by the critical (sonic) velocity, whatever the pressure drop (see Volume 1, Chapter 4). The design of venting systems to give adequate protection against over-pressure is a complex and difficult subject, particularly if two-phase flow is likely to occur. For complete protection the venting system must be capable of venting at the same rate as the vapour is being generated. For reactors, the maximum rate of vapour generation resulting from a loss of control can usually be estimated. Vessels must also be protected against over-pressure caused by external fires. In these circumstances the maximum rate of vapour generation will depend on the rate of heating. Standard formulae are available for the estimation of the maximum rates of heat input and relief rates, see ROSPA (1971) and NFPA (1987a,b).

For some vessels, particularly where complex vent piping systems are needed, it may be impractical for the size of the vent to give complete protection against the worst possible situation.

For a comprehensive discussion of the problem of vent system design, and the design methods available, see the papers by Duxbury (1976, 1979).

The design of relief systems has been studied by the Design Institute for Emergency Relief Systems (DIERS), established by the American Institute of Chemical Engineers; Fisher (1985). DIERS has published recommended design methods; see Poole (1985) and AIChE (1992a,b). Computer programs based on the work by DIERS are also available.

## ***Under-pressure (vacuum)***

Unless designed to withstand external pressure (see Chapter 13) a vessel must be protected against the hazard of under-pressure, as well as over-pressure. Under-pressure will normally mean vacuum on the inside with atmospheric pressure on the outside. It requires only a slight drop in pressure below atmospheric pressure to collapse a storage tank. Though the pressure differential may be small, the force on the tank roof will be considerable. For example, if the pressure in a 10-m diameter tank falls to 10 millibars below the external pressure, the total load on the tank roof will be around 80,000 N (8 tonne). It is not an uncommon occurrence for a storage tank to be sucked in (collapsed) by the suction pulled by the discharge pump, due to the tank vents having become blocked. Where practical, vacuum breakers (valves that open to atmosphere when the internal pressure drops below atmospheric) should be fitted.

### **9.3.7. Temperature deviations**

Excessively high temperature, over and above that for which the equipment was designed, can cause structural failure and initiate a disaster. High temperatures can arise from loss

of control of reactors and heaters; and, externally, from open fires. In the design of processes where high temperatures are a hazard, protection against high temperatures is provided by:

1. Provision of high-temperature alarms and interlocks to shut down reactor feeds, or heating systems, if the temperature exceeds critical limits.
2. Provision of emergency cooling systems for reactors, where heat continues to be generated after shut-down; for instance, in some polymerisation systems.
3. Structural design of equipment to withstand the worst possible temperature excursion.
4. The selection of intrinsically safe heating systems for hazardous materials.

Steam, and other vapour heating systems, are intrinsically safe; as the temperature cannot exceed the saturation temperature at the supply pressure. Other heating systems rely on control of the heating rate to limit the maximum process temperature. Electrical heating systems can be particularly hazardous.

### ***Fire protection***

To protect against structural failure, water-deluge systems are usually installed to keep vessels and structural steelwork cool in a fire.

The lower section of structural steel columns are also often lagged with concrete or other suitable materials.

### **9.3.8. Noise**

Excessive noise is a hazard to health and safety. Long exposure to high noise levels can cause permanent damage to hearing. At lower levels, noise is a distraction and causes fatigue.

The unit of sound measurement is the decibel, defined by the expression:

$$\text{Sound level} = 20 \log_{10} \left[ \frac{\text{RMS sound pressure (Pa)}}{2 \times 10^{-5}} \right], \text{ dB} \quad (9.1)$$

The subjective effect of sound depends on frequency as well as intensity.

Industrial sound meters include a filter network to give the meter a response that corresponds roughly to that of the human ear. This is termed the “A” weighting network and the readings are reported as dB(A).

Permanent damage to hearing can be caused at sound levels above about 90 dB(A), and it is normal practice to provide ear protection in areas where the level is above 80 dB(A).

Excessive plant noise can lead to complaints from neighbouring factories and local residents. Due attention should be given to noise levels when specifying, and when laying out, equipment that is likely to be excessively noisy; such as, compressors, fans, burners and steam relief valves.

Several books are available on the general subject of industrial noise control, Bias and Hansen (2003), and on noise control in the process industries, Cheremisnoff (1996), ASME (1993).

## 9.4. DOW FIRE AND EXPLOSION INDEX

The hazard classification guide developed by the Dow Chemical Company and published by the American Institute of Chemical Engineering, Dow (1994) ([www.aiche.org](http://www.aiche.org)), gives a method of evaluating the potential risk from a process, and assessing the potential loss.

A numerical “Fire and explosion index” (F & EI) is calculated, based on the nature of the process and the properties of the process materials. The larger the value of the F & EI, the more hazardous the process, see Table 9.3.

Table 9.3. Assessment of hazard

Fire and explosion index range	Degree of hazard
1–60	Light
61–96	Moderate
97–127	Intermediate
128–158	Heavy
>159	Severe

Adapted from the Dow F & EI guide (1994).

To assess the potential hazard of a new plant, the index can be calculated after the Piping and Instrumentation and equipment layout diagrams have been prepared. In earlier versions of the guide the index was then used to determine what preventative and protection measures were needed, see Dow (1973). In the current version the preventative and protection measures, that have been incorporated in the plant design to reduce the hazard—are taken into account when assessing the potential loss; in the form of loss control credit factors.

It is worthwhile estimating the F & EI index at an early stage in the process design, as it will indicate whether alternative, less hazardous, process routes should be considered.

Only a brief outline of the method used to calculate the Dow F & EI will be given in this section. The full guide should be studied before applying the technique to a particular process. Judgement, based on experience with similar processes, is needed to decide the magnitude of the various factors used in the calculation of the index, and the loss control credit factors.

### 9.4.1. Calculation of the Dow F & EI

The procedure for calculating the index and the potential loss is set out in Figure 9.1.

The first step is to identify the units that would have the greatest impact on the magnitude of any fire or explosion. The index is calculated for each of these units.

The basis of the F & EI is a *Material Factor* (MF). The MF is then multiplied by a *Unit Hazard Factor*,  $F_3$ , to determine the F & EI for the process unit. The Unit Hazard factor is the product of two factors which take account of the hazards inherent in the operation of the particular process unit: the general and special process hazards, see Figure 9.2.

#### **Material factor**

The material factor is a measure of the intrinsic rate of energy release from the burning, explosion, or other chemical reaction of the material. Values for the MF for over 300 of

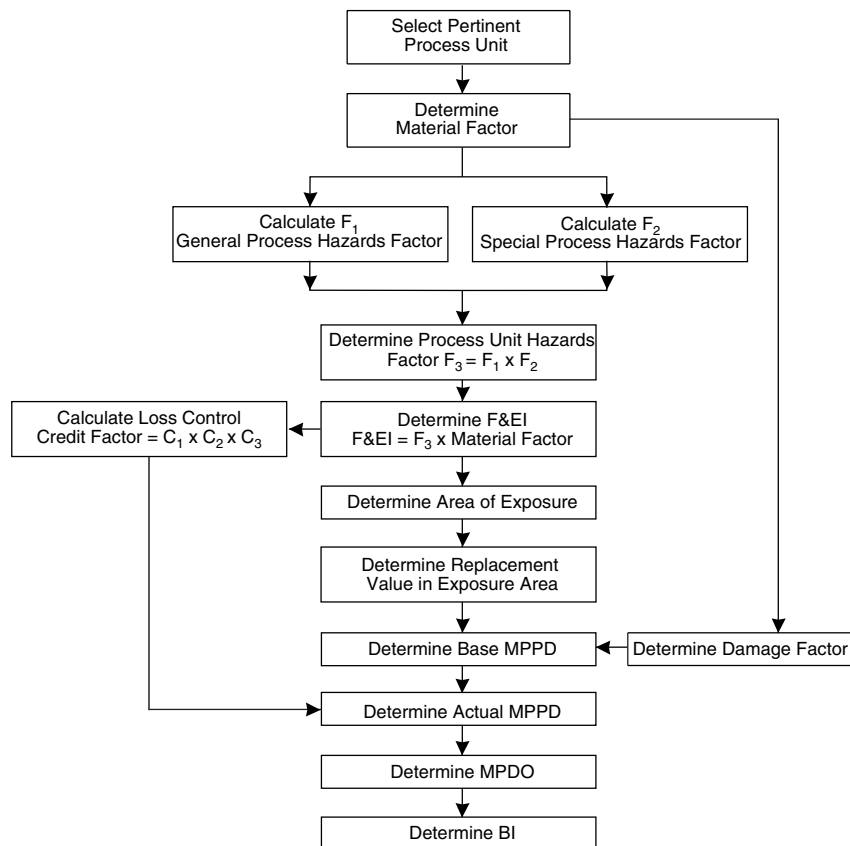


Figure 9.1. Procedure for calculating the fire and explosion index and other risk analysis information. From Dow (1994) reproduced by permission of the American Institute of Chemical Engineers. © 1994 AIChE. All rights reserved.

the most commonly used substances are given in the guide. The guide also includes a procedure for calculating the MF for substances not listed: from a knowledge of the flash points, (for dusts, dust explosion tests) and a reactivity value,  $N_r$ . The reactivity value is a qualitative description of the reactivity of the substance, and ranges from 0 for stable substances, to 4 for substances that are capable of unconfined detonation.

Some typical material factors are given in Table 9.4.

In calculating the F & EI for a unit the value for the material with the highest MF, which is present in significant quantities, is used.

### **General process hazards**

The general process hazards are factors that play a primary role in determining the magnitude of the loss following an incident.

Six factors are listed on the calculation form, Figure 9.2.

Table 9.4. Some typical material factors

	MF	Flash point°C	Heat of combustion MJ/kg
Acetaldehyde	24	-39	24.4
Acetone	16	-20	28.6
Acetylene	40	gas	48.2
Ammonia	4	gas	18.6
Benzene	16	-11	40.2
Butane	21	gas	45.8
Chlorine	1	—	0.0
Cyclohexane	16	-20	43.5
Ethyl alcohol	16	13	26.8
Hydrogen	21	gas	120.0
Nitroglycerine	40	—	18.2
Sulphur	4	—	9.3
Toluene	16	40	31.3
Vinyl Chloride	21	gas	18.6

- A. *Exothermic chemical reactions*: the penalty varies from 0.3 for a mild exotherm, such as hydrogenation, to 1.25 for a particularly sensitive exotherm, such as nitration.
- B. *Endothermic processes*: a penalty of 0.2 is applied to reactors, only. It is increased to 0.4 if the reactor is heated by the combustion of a fuel.
- C. *Materials handling and transfer*: this penalty takes account of the hazard involved in the handling, transfer and warehousing of the material.
- D. *Enclosed or indoor process units*: accounts for the additional hazard where ventilation is restricted.
- E. *Access of emergency equipment*: areas not having adequate access are penalised. Minimum requirement is access from two sides.
- F. *Drainage and spill control*: penalises design conditions that would cause large spills of flammable material adjacent to process equipment; such as inadequate design of drainage.

### **Special process hazards**

The special process hazards are factors that are known from experience to contribute to the probability of an incident involving loss.

Twelve factors are listed on the calculation form, Figure 9.2.

- A. *Toxic materials*: the presence of toxic substances after an incident will make the task of the emergency personnel more difficult. The factor applied ranges from 0 for non-toxic materials, to 0.8 for substances that can cause death after short exposure.
- B. *Sub-atmospheric pressure*: allows for the hazard of air leakage into equipment. It is only applied for pressure less than 500 mmHg (9.5 bara).
- C. *Operation in or near flammable range*: covers for the possibility of air mixing with material in equipment or storage tanks, under conditions where the mixture will be within the explosive range.



- D. *Dust explosion*: covers for the possibility of a dust explosion. The degree of risk is largely determined by the particle size. The penalty factor varies from 0.25 for particles above 175  $\mu\text{m}$ , to 2.0 for particles below 75  $\mu\text{m}$ .
- E. *Relief pressure*: this penalty accounts for the effect of pressure on the rate of leakage, should a leak occur. Equipment design and operation becomes more critical as the operating pressure is increased. The factor to apply depends on the relief device setting and the physical nature of the process material. It is determined from Figure 2 in the Dow Guide.
- F. *Low temperature*: this factor allows for the possibility of brittle fracture occurring in carbon steel, or other metals, at low temperatures (see Chapter 7 of this book).
- G. *Quantity of flammable material*: the potential loss will be greater the greater the quantity of hazardous material in the process or in storage. The factor to apply depends on the physical state and hazardous nature of the process material, and the quantity of material. It varies from 0.1 to 3.0, and is determined from Figures 3, 4 and 5 in the Dow Guide.
- H. *Corrosion and erosion*: despite good design and materials selection, some corrosion problems may arise, both internally and externally. The factor to be applied depends on the anticipated corrosion rate. The severest factor is applied if stress corrosion cracking is likely to occur (see Chapter 7 of this book).
- I. *Leakage—joints and packing*: this factor accounts for the possibility of leakage from gaskets, pump and other shaft seals, and packed glands. The factor varies from 0.1 where there is the possibility of minor leaks, to 1.5 for processes that have sight glasses, bellows or other expansion joints.
- J. *Use of fired heaters*: the presence of boilers or furnaces, heated by the combustion of fuels, increases the probability of ignition should a leak of flammable material occur from a process unit. The risk involved will depend on the siting of the fired equipment and the flash point of the process material. The factor to apply is determined with reference to Figure 6 in the Dow Guide.
- K. *Hot oil heat exchange system*: most special heat exchange fluids are flammable and are often used above their flash points; so their use in a unit increases the risk of fire or explosion. The factor to apply depends on the quantity and whether the fluid is above or below its flash point; see Table 5 in the Guide.
- L. *Rotating equipment*: this factor accounts for the hazard arising from the use of large pieces of rotating equipment: compressors, centrifuges, and some mixers.

#### 9.4.2 Potential loss

The procedure for estimating the potential loss that would follow an incident is set out in Table 9.5: the Unit analysis summary.

The first step is to calculate the *Damage factor* for the unit. The Damage factor depends on the value of the Material factor and the Process unit hazards factor ( $F_3$  in Figure 2). It is determined using Figure 8 in the Dow Guide.

An estimate is then made of the area (radius) of exposure. This represents the area containing equipment that could be damaged following a fire or explosion in the unit being considered. It is evaluated from Figure 7 in the Guide and is a linear function of the Fire and Explosion Index.



Table 9.5. Loss control credit factors

1. Process Control Credit Factor ( $C_1$ )

Feature	Credit Factor Range	Credit Factor Used(2)	Feature	Credit Factor Range	Credit Factor Used(2)
a. Emergency Power	0.98		f. Inert Gas	0.94 to 0.96	
b. Cooling	0.97 to 0.99		g. Operating Instructions/Procedures	0.91 to 0.99	
c. Explosion Control	0.84 to 0.98		h. Reactive Chemical Review	0.91 to 0.98	
d. Emergency Shutdown	0.96 to 0.99		i. Other Process Hazard Analysis	0.91 to 0.98	
e. Computer Control	0.93 to 0.99				

$C_1$  Value(3)

2. Material Isolation Credit Factor ( $C_2$ )

Feature	Credit Factor Range	Credit Factor Used(2)	Feature	Credit Factor Range	Credit Factor Used(2)
a. Remote Control Valves	0.96 to 0.98		c. Drainage	0.91 to 0.97	
b. Dump/Blowdown	0.96 to 0.98		d. Interlock	0.98	

$C_2$  Value(3)

3. Fire Protection Credit Factor ( $C_3$ )

Feature	Credit Factor Range	Credit Factor Used(2)	Feature	Credit Factor Range	Credit Factor Used(2)
a. Leak Detection	0.94 to 0.98		f. Water Curtains	0.97 to 0.98	
b. Structural Steel	0.95 to 0.98		g. Foam	0.92 to 0.97	
c. Fire Water Supply	0.94 to 0.97		h. Hand Extinguishers/Monitors	0.93 to 0.98	
d. Special Systems	0.91		i. Cable Protection	0.94 to 0.98	
e. Sprinkler Systems	0.74 to 0.97				

$C_3$  Value(3)

Loss Control Credit Factor =  $C_1 \times C_2 \times C_3(3) =$   (enter on line 7 Table 9.6)

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An estimate of the replacement value of the equipment within the exposed area is then made, and combined with by the damage factor to estimate the *Base maximum probable property damage* (Base MPPD).

The *Maximum probable property damage* (MPPD) is then calculated by multiplying the Base MPPD by a *Credit control factor*. The Loss control credit control factors, see Table 9.6, allow for the reduction in the potential loss given by the preventative and protective measures incorporated in the design.

The MPPD is used to predict the maximum number of days which the plant will be down for repair, the *Maximum probable days outage* (MPDO). The MPDO is used to estimate

Table 9.6. Process unit risk analysis Summary

1. Fire & Explosion Index (F&EI) . . . . .		
2. Radius of Exposure . . . . . (Figure 7)*	ft or m	
3. Area of Exposure . . . . .	ft <sup>2</sup> or m <sup>2</sup>	
4. Value of Area of Exposure . . . . .		\$MM
5. Damage Factor . . . . . (Figure 8)*		
6. Base Maximum Probable Property Damage—(Base MPPD) [4 × 5] . . . . .		\$MM
7. Loss Control Credit Factor . . . . . (See Above)		
8. Actual Maximum Probable Property Damage—(Actual MPPD) [6 × 7] . . . . .		\$MM
9. Maximum Probable Days Outage—(MPDO) . . . . . (Figure 9)*	days	
10. Business Interruption—(BI) . . . . .		\$MM

(2) For no credit factor enter 1.00. (3) Product of all factors used.

\*Refer to *Fire & Explosion Index Hazard Classification Guide* for details.

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the financial loss due to the lost production: the *Business interruption* (BI). The financial loss due to lost business opportunity can often exceed the loss from property damage.

### 9.4.3. Basic preventative and protective measures

The basic safety and fire protective measures that should be included in all chemical process designs are listed below. This list is based on that given in the Dow Guide, with some minor amendments.

1. Adequate, and secure, water supplies for fire fighting.
2. Correct structural design of vessels, piping, steel work.
3. Pressure-relief devices.
4. Corrosion-resistant materials, and/or adequate corrosion allowances.
5. Segregation of reactive materials.
6. Earthing of electrical equipment.
7. Safe location of auxiliary electrical equipment, transformers, switch gear.
8. Provision of back-up utility supplies and services.
9. Compliance with national codes and standards.
10. Fail-safe instrumentation.
11. Provision for access of emergency vehicles and the evacuation of personnel.
12. Adequate drainage for spills and fire-fighting water.
13. Insulation of hot surfaces.
14. No glass equipment used for flammable or hazardous materials, unless no suitable alternative is available.
15. Adequate separation of hazardous equipment.
16. Protection of pipe racks and cable trays from fire.
17. Provision of block valves on lines to main processing areas.
18. Protection of fired equipment (heaters, furnaces) against accidental explosion and fire.
19. Safe design and location of control rooms.

*Note:* the design and location of control rooms, particularly as regards protection against an unconfined vapour explosion, is covered in a publication of the Chemical Industries Association, CIA (1979a).

#### **9.4.4. Mond fire, explosion, and toxicity index**

The Mond index was developed from the Dow F and E index by personnel at the ICI Mond division. The third edition of the Dow index, Dow (1973), was extended to cover a wider range of process and storage installations; the processing of chemicals with explosive properties; and the evaluation of a toxicity hazards index. Also included was a procedure to allow for the off-setting effects of good design, and of control and safety instrumentation. Their revised, Mond fire, explosion and toxicity index was discussed in a series of papers by Lewis (1979a, 1979b); which included a technical manual setting out the calculation procedure. An extended version of the manual was issued in 1985, and an amended version published in 1993, ICI (1993).

##### ***Procedure***

The basic procedures for calculating the Mond indices are similar to those used for the Dow index.

The process is first divided into a number of units which are assessed individually.

The dominant material for each unit is then selected and its material factor determined. The material factor in the Mond index is a function of the energy content per unit weight (the heat of combustion).

The material factor is then modified to allow for the effect of general and special process and material hazards; the physical quantity of the material in the process step; the plant layout; and the toxicity of process materials.

Separate fire and explosion indices are calculated. An aerial explosion index can also be estimated, to assess the potential hazard of aerial explosions. An equivalent Dow index can also be determined.

The individual fire and explosion indexes are combined to give an overall index for the process unit. The overall index is the most important in assessing the potential hazard.

The magnitude of the potential hazard is determined by reference to rating tables, similar to that shown for the Dow index in Table 9.2.

After the initial calculation of the indices (the initial indices), the process is reviewed to see what measures can be taken to reduce the rating (the potential hazard).

The appropriate off-setting factors to allow for the preventative features included in the design are then applied, and final hazard indices calculated.

##### ***Preventative measures***

Preventative measures fall into two categories:

1. Those that reduce the number of incidents. Such as: sound mechanical design of equipment and piping; operating and maintenance procedures, and operator training.
2. Those that reduce the scale of a potential incident; such as: measures for fire protection, and fixed fire fighting equipment.

Many measures will not fit neatly into individual categories but will apply to both.

## Implementation

The Mond technique of hazard evaluation is fully explained in the ICI technical manual, ICI (1993)<sup>(1)</sup>, to which reference should be made to implement the method. The calculations are made using a standard form, similar to that used for the Dow index. A computer program is available for use with IBM compatible personal computers.

### 9.4.5. Summary

The Dow and Mond indexes are useful techniques, which can be used in the early stages of a project design to evaluate the hazards and risks of the proposed process.

Calculation of the indexes for the various sections of the process will highlight any particularly hazardous sections and indicate where a detailed study is needed to reduce the hazards.

#### Example 9.1

Evaluate the Dow F & EI for the nitric acid plant described in Chapter 4, Example 4.4.

#### Solution

The calculation is set out on the special form shown in Figure 9.2a. Notes on the decisions taken and the factors used are given below.

*Unit:* consider the total plant, no separate areas, but exclude the main storages.

*Material factor:* for ammonia, from Dow Guide, and Table 9.3.

$$MF = 4.0$$

*Note:* Hydrogen is present, and has a larger material factor (21) but the concentration is too small for it to be considered the dominant material.

#### General process hazards:

- A. Oxidising reaction, factor = 0.5
- B. Not applicable.
- C. Not applicable.
- D. Not applicable.
- E. Adequate access would be provided, factor = 0.0.
- F. Adequate drainage would be provided, factor = 0.0.

#### Special process hazards:

- A. Ammonia is highly toxic, likely to cause serious injury, factor = 0.6.
- B. Not applicable.

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<sup>(1)</sup> Published under licence from Imperial Chemical Industries plc by Dr P. Doran and T. R. Greig, 40 Mors Lane, Northwich, Cheshire, CW8 2PX, United Kingdom.

## FIRE &amp; EXPLOSION INDEX

AREA/COUNTRY	DIVISION	LOCATION	SLIGO	DATE	20 JAN 1997
SITE	MANUFACTURING UNIT NITRIC ACID	PROCESS UNIT	COMPLETE PLANT		
PREPARED BY: RKS	APPROVED BY:(Superintendent) ANOTHER		BUILDING		
REVIEWED BY:(Management)	REVIEWED BY:(Technology Center)		REVIEWED BY:(Safety & Loss Prevention)		
MATERIALS IN PROCESS UNIT AMMONIA, AIR, OXIDES OF NITROGEN, WATER					
STATE OF OPERATION — DESIGN — START UP <input checked="" type="checkbox"/> NORMAL OPERATION — SHUTDOWN			BASIC MATERIAL(S) FOR MATERIAL FACTOR AMMONIA		
MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 °F (60 °C)					4
<b>1. General Process Hazards</b>				<b>Penalty Factor Range</b>	<b>Penalty Factor Used(1)</b>
<b>Base Factor</b> .....				1.00	1.00
A. Exothermic Chemical Reactions				0.30 to 1.25	0.50
B. Endothermic Processes				0.20 to 0.40	
C. Material Handling and Transfer				0.25 to 1.05	
D. Enclosed or Indoor Process Units				0.25 to 0.90	
E. Access				0.20 to 0.35	
F. Drainage and Spill Control _____ gal or cu.m.				0.25 to 0.50	
<b>General Process Hazards Factor (F<sub>1</sub>)</b> .....				1.50	
<b>2. Special Process Hazards</b>					
<b>Base Factor</b> .....				1.00	1.00
A. Toxic Material(s)				0.20 to 0.80	0.60
B. Sub-Atmospheric Pressure (< 500 mm Hg)				0.50	
C. Operation In or Near Flammable Range _____ Inerted _____ Not Inerted					
1. Tank Farms Storage Flammable Liquids				0.50	
2. Process Upset or Purge Failure				0.30	0.80
3. Always in Flammable Range				0.80	
D. Dust Explosion (See Table 3)				0.25 to 2.00	
E. Pressure (See Figure 2) Operating Pressure <u>103</u> psig or kPa gauge Relief Setting <u>125</u> psig or kPa gauge					0.35
F. Low Temperature				0.20 to 0.30	
G. Quantity of Flammable/Unstable Material: Quantity _____ lb or kg H <sub>C</sub> = _____ BTU/lb or kcal/kg					
1. Liquids or Gases in Process (See Figure 3)					
2. Liquids or Gases in Storage (See Figure 4)					
3. Combustible Solids in Storage, Dust in Process (See Figure 5)					
H. Corrosion and Erosion				0.10 to 0.75	0.10
I. Leakage – Joints and Packing				0.10 to 1.50	0.10
J. Use of Fired Equipment (See Figure 6)					
K. Hot Oil Heat Exchange System (See Table 5)				0.15 to 1.15	
L. Rotating Equipment				0.50	<b>0.30</b>
<b>Special Process Hazards Factor (F<sub>2</sub>)</b> .....				3.45	
<b>Process Unit Hazards Factor (F<sub>1</sub> x F<sub>2</sub>) = F<sub>3</sub></b> .....				5.20	
<b>Fire and Explosion Index (F<sub>3</sub> x MF = F&amp;EI)</b> .....				<b>21</b>	

(1) For no penalty use 0.00.

Figure 9.2a. Fire and explosion index calculation form, Example 9.1.

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- C. Operation always is within the flammable limits, factor = 0.8.
- D. Not applicable.
- E. Operation pressure  $8 \text{ atm} = 8 \times 14.7 - 14.7 = 103 \text{ psig}$ . Set relief valve at 20% above the operating pressure (see Chapter 13 of this book) = 125 psig.  
From Figure 2 in the guide, factor = 0.35.  
*Note:* psig = pounds force per square inch, gauge.
- F. Not applicable.
- G. The largest quantity of ammonia in the process will be the liquid in the vaporiser, say around 500 kg.  
Heat of combustion, Table 9.3 = 18.6 MJ/kg  
Potential energy release =  $500 \times 18.6 = 9300 \text{ MJ}$   
 $= 9300 \times 10^6 / (1.05506 \times 10^3) = 8.81 \times 10^6 \text{ Btu}$   
which is too small to register on Figure 3 in the Guide, factor = 0.0.
- H. Corrosion resistant materials of construction would be specified, but external corrosion is possible due to nitric oxide fumes, allow minimum factor = 0.1.
- I. Welded joints would be used on ammonia service and mechanical seals on pumps.  
Use minimum factor as full equipment details are not known at the flow-sheet stage, factor = 0.1.
- J. Not applicable.
- K. Not applicable.
- L. Large turbines and compressors used, factor = 0.5.

The index works out at 21: classified as “Light”. Ammonia would not normally be considered a dangerously flammable material; the danger of an internal explosion in the reactor is the main process hazard. The toxicity of ammonia and the corrosiveness of nitric acid would also need to be considered in a full hazard evaluation.

## 9.5. HAZARD AND OPERABILITY STUDIES

A hazard and operability study is a procedure for the systematic, critical, examination of the operability of a process. When applied to a process design or an operating plant, it indicates potential hazards that may arise from deviations from the intended design conditions.

The technique was developed by the Petrochemicals Division of Imperial Chemical Industries, see Lawley (1974), and is now in general use in the chemical and process industries.

The term “operability study” should more properly be used for this type of study, though it is usually referred to as a hazard and operability study, or HAZOP study. This can cause confusion with the term “hazard analysis”, which is a technique for the quantitative assessment of a hazard, after it has been identified by an operability study, or similar technique. Numerous books have been written illustrating the use of HAZOP. Those by Hyatt (2003), AIChE (2000), Taylor (2000) and Kletz (1999a) give comprehensive descriptions of the technique, with examples.

A brief outline of the technique is given in this section to illustrate its use in process design. It can be used to make a preliminary examination of the design at the flow-sheet stage; and for a detailed study at a later stage, when a full process description, final flow-sheets, P and I diagrams, and equipment details are available.

### 9.5.1. Basic principles

A formal operability study is the systematic study of the design, vessel by vessel, and line by line, using “guide words” to help generate thought about the way deviations from the intended operating conditions can cause hazardous situations.

The seven guide words recommended in the CIA booklet are given in Table 9.7. In addition to these words, the following words are also used in a special way, and have the precise meanings given below:

*Intention:* the intention defines how the particular part of the process was intended to operate; the intention of the designer.

*Deviations:* these are departures from the designer’s intention which are detected by the systematic application of the guide words.

*Causes:* reasons why, and how, the deviations could occur. Only if a deviation can be shown to have a realistic cause is it treated as meaningful.

*Consequences:* the results that follow from the occurrence of a meaningful deviation.

*Hazards:* consequences that can cause damage (loss) or injury.

The use of the guide words can be illustrated by considering a simple example. Figure 9.3 shows a chlorine vaporiser, which supplies chlorine at 2 bar to a chlorination reactor. The vaporiser is heated by condensing steam.

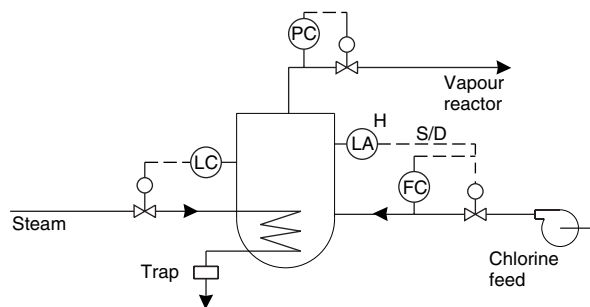


Figure 9.3. Chlorine vaporiser instrumentation

Consider the steam supply line and associated control instrumentation. The designer’s intention is that steam shall be supplied at a pressure and flow rate to match the required chlorine demand.

Apply the guide word No:

Possible deviation — no steam flow.

Possible causes—blockage, valve failure (mechanical or power), failure of steam supply (fracture of main, boiler shut-down).

Clearly this is a meaningful deviation, with several plausible causes.

Consequences—the main consequence is loss of chlorine flow to the chlorination reactor.

The effect of this on the reactor operation would have to be considered. This would be brought out in the operability study on the reactor; it would be a possible cause of no chlorine flow.

Apply the guide word MORE:

Possible deviation—more steam flow.

Possible cause—valve stuck open.

Consequences—low level in vaporiser (this should activate the low level alarm), higher rate of flow to the reactor.

*Note:* to some extent the level will be self-regulating, as the level falls the heating surface is uncovered.

Hazard—depends on the possible effect of high flow on the reactor.

Possible deviation—more steam pressure (increase in mains pressure).

Possible causes—failure of pressure-regulating valves.

Consequences—increase in vaporisation rate. Need to consider the consequences of the heating coil reaching the maximum possible steam system pressure.

Hazard—rupture of lines (unlikely), effect of sudden increase in chlorine flow on reactor.

### 9.5.2. Explanation of guide words

The basic meaning of the guide words in Table 9.7. The meaning of the words No/Not, MORE and LESS are easily understood; the NO/NOT, MORE and LESS could, for example, refer to flow, pressure, temperature, level and viscosity. All circumstances leading to No flow should be considered, including reverse flow.

The other words need some further explanation:

**AS WELL AS:** something in addition to the design intention; such as, impurities, side-reactions, ingress of air, extra phases present.

**PART OF:** something missing, only part of the intention realized; such as, the change in composition of a stream, a missing component.

**REVERSE:** the reverse of, or opposite to, the design intention. This could mean reverse flow if the intention was to transfer material. For a reaction, it could mean the reverse reaction. In heat transfer, it could mean the transfer of heat in the opposite direction to what was intended.

**OTHER THAN:** an important and far-reaching guide word, but consequently more vague in its application. It covers all conceivable situations other than that intended; such as, start-up, shut-down, maintenance, catalyst regeneration and charging, failure of plant services.

When referring to time, the guide words SOONER THAN and LATER THAN can also be used.



Table 9.7. A list of guide words

Guide words	Meanings	Comments
NO or NOT	The complete negation of these intentions	No part of the intentions is achieved but nothing else happens
MORE	Quantitative increases or decreases	These refer to quantities and properties such as flow rates and temperatures, as well as activities like "HEAT" and "REACT"
LESS		
AS WELL AS	A qualitative increase	All the design and operating intentions are achieved together with some additional activity
PART OF	A qualitative decrease	Only some of the intentions are achieved; some are not
REVERSE	The logical opposite of the intention	This is mostly applicable to activities, for example reverse flow or chemical reaction. It can also be applied to substances, e.g. "POISON" instead of "ANTIDOTE" or "D" instead of "L" optical isomers
OTHER THAN	Complete substitution	No part of the original intention is achieved. Something quite different happens

### 9.5.3. Procedure

An operability study would normally be carried out by a team of experienced people, who have complementary skills and knowledge; led by a team leader who is experienced in the technique.

The team examines the process vessel by vessel, and line by line, using the guide words to detect any hazards.

The information required for the study will depend on the extent of the investigation.

A preliminary study can be made from a description of the process and the process flow-sheets. For a detailed, final, study of the design, the flow-sheets, piping and instrument diagrams, equipment specifications and layout drawings would be needed. For a batch process information on the sequence of operation will also be required, such as that given in operating instructions, logic diagrams and flow charts.

A typical sequence of events is shown in Figure 9.4. After each line has been studied it is marked on the flow-sheet as checked.

A written record is not normally made of each step in the study, only those deviations that lead to a potential hazard are recorded. If possible, the action needed to remove the hazard is decided by the team and recorded. If more information, or time, is needed to decide the best action, the matter is referred to the design group for action, or taken up at another meeting of the study team.

When using the operability study technique to vet a process design, the action to be taken to deal with a potential hazard will often be modifications to the control systems and instrumentation: the inclusion of additional alarms, trips, or interlocks. If major hazards

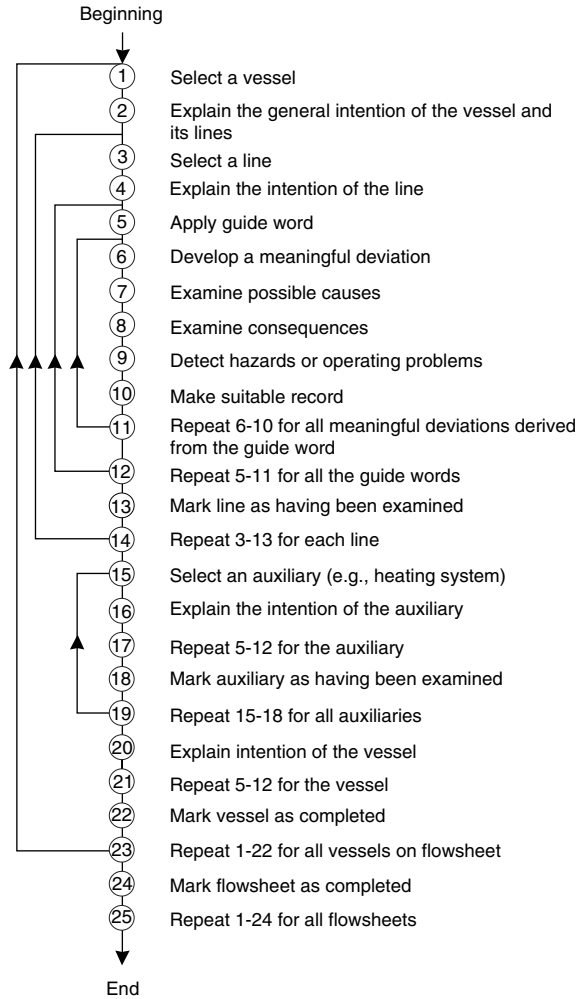
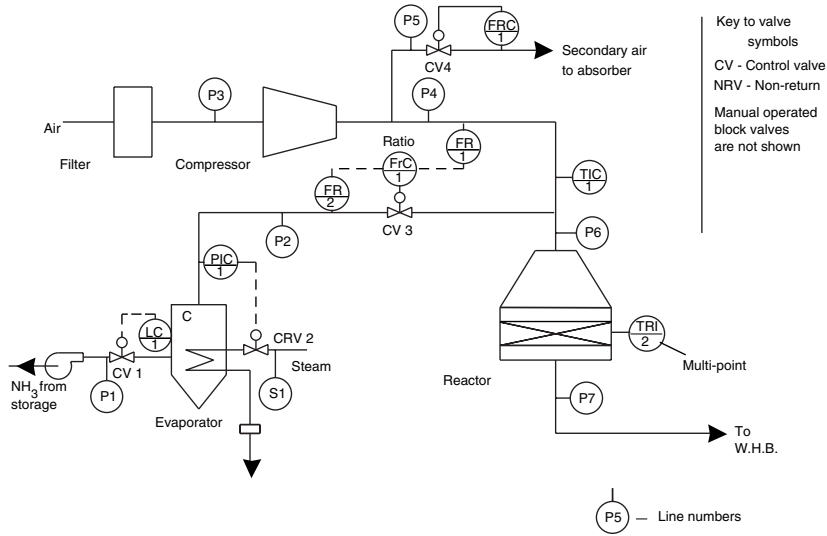


Figure 9.4. Detailed sequence of an operability study

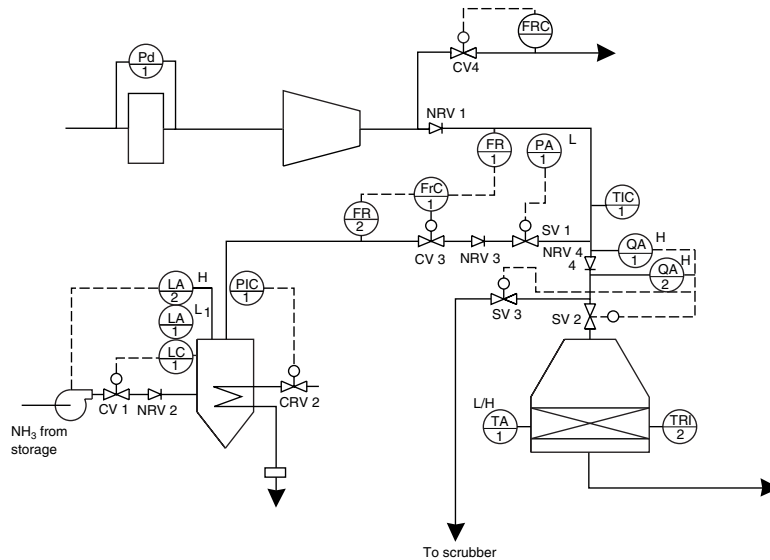
are identified, major design changes may be necessary; alternative processes, materials or equipment.

### Example 9.2

This example illustrates how the techniques used in an operability study can be used to decide the instrumentation required for safe operation. Figure 9.5a shows the basic instrumentation and control systems required for the steady-state operation of the reactor section of the nitric acid process considered in Example 4.4. Figure 9.5b shows the



(a)



(b)

Figure 9.5. Nitric acid plant, reactor section (a) basic instrumentation (b) full instrumentation

additional instrumentation and safety trips added after making the operability study set out below. The instrument symbols used are explained in Chapter 5.

The most significant hazard of this process is the probability of an explosion if the concentration of ammonia in the reactor is inadvertently allowed to reach the explosive range, >14 per cent.

**Operability study**

The sequence of steps shown in Figure 9.4 is followed. Only deviations leading to action, and those having consequences of interest, are recorded.

**Vessel – Air Filter**

Intention – to remove particles that would foul the reactor catalyst

Guide word	Deviation	Cause	Consequences and action
<i>Line No. P3</i>			
Intention – transfers clear air at atmospheric pressure and ambient temperature to compressor			
LESS OF	Flow	Partially blocked filter	Possible dangerous increase in NH <sub>3</sub> concentration: measure and log pressure differential
AS WELL AS	Composition	Filter damaged, incorrectly installed	Impurities, possible poisoning of catalyst: proper maintenance

**Vessel – Compressor**

Intention – to supply air at 8 bar, 12,000 kg/h, 250°C, to the mixing tee

*Line No. P4*

Intention – transfers air to reactor (mixing tee)

NO/NONE	Flow	Compressor failure	Possible dangerous NH <sub>3</sub> conc.: low flow pressure alarm (PA1) interlocked to shut-down NH <sub>3</sub> flow
MORE	Flow	Failure of compressor controls	High rate of reaction, high reactor temperature: high-temperature alarms (TA1)
REVERSE	Flow	Fall in line press. (compressor fails) high pressure at reactor	NH <sub>3</sub> in compressor – explosion hazard: fit non-return valve (NRV1); hot wet acid gas-corrosion; fit second valve (NRV4)

*Line No. P5*

Intention – transfer secondary air to absorber

NO	Flow	Compressor failure CV4 failure	Incomplete oxidation, air pollution from absorber vent: operating procedures
LESS	Flow	CV4 pluggage FRC1 failure	As no flow

**Vessel – Ammonia vaporiser**

Intention – evaporate liquid ammonia at 8 bar, 25°C, 731 kg/h

Guide word	Deviation	Cause	Consequences and action
<i>Line No. P1</i>			
Intention – transfer liquid NH <sub>3</sub> from storage			
NO	Flow	Pump failure CV1 fails	Level falls in vaporiser: fit low-level alarm (LA1)
LESS	Flow	Partial failure pump/valve	(LA1) alarms
MORE	Flow	CV1 sticking, LC1 fails	Vaporiser floods, liquid to reactor: fit high-level alarm (LA2) with automatic pump shut-down
AS WELL AS	Water brine	Leakage into storages from refrigeration	Concentration of NH <sub>4</sub> OH in vaporiser: routine analysis, maintenance
REVERSE	Flow	Pump fails, vaporiser press. higher than delivery	Flow of vapour into storages: (LA1) alarms; fit non-return valve (NRV2)
<i>Line No. P2</i>			
Intention – transfers vapour to mixing tee			
NO	Flow	Failure of steam flow, CV3 fails closed	(LA1) alarms, reaction ceases: considered low flow alarm, rejected – needs resetting at each rate
LESS	Flow	Partial failure or blockage CV3	As no flow
MORE	Level	LC1 fails	LA2 alarms
	Flow	FR2/ratio control mis-operation	Danger of high ammonia concentration: fit alarm, fit analysers (duplicate) with high alarm 12 per cent NH <sub>3</sub> (QA1, QA2)
REVERSE	Level	LC1 fails	LA2 alarms
	Flow	Steam failure	Hot, acid gases from reactor – corrosion: fit non-return valve (NRV3)
Line S1 (auxiliary)		CRV2 fails, trap frozen	High level in vaporiser: LA2 actuated

Guide word	Deviation	Cause	Consequences and action
<i>Vessel – Reactor</i>			
Intention – oxidises NH <sub>3</sub> with air, 8 bar, 900°C			
<i>Line No. P6</i>			
Intention – transfers mixture to reactor, 250°C			
NO	Flow	NRV4 stuck closed	Fall in reaction rate: fit low temp. alarm (TA1)
LESS	Flow NH <sub>3</sub> conc.	NRV4 partially closed Failure of ratio control	AS NO Temperatures fall: TA1 alarms (consider low conc. alarm on QA1, 2)
MORE	NH <sub>3</sub> conc.	Failure of ratio control, air flow restricted	High reactor temp.: TA1 alarms 14 per cent explosive mixture enters reactor – disaster: include automatic shut-down by-pass actuated by QA1, 2, SV2, SV3
	Flow	Control systems failure	High reactor temp.: TA1 alarms
<i>Line No. P7</i>			
Intention – transfers reactor products to waste-heat boiler			
AS WELL AS	Composition	Refractory particles from reactor	Possible pluggage of boiler tubes: install filter up-stream of boiler

## 9.6. HAZARD ANALYSIS

An operability study will identify potential hazards, but gives no guidance on the likelihood of an incident occurring, or the loss suffered; this is left to the intuition of the team members. Incidents usually occur through the coincident failure of two or more items; failure of equipment, control systems and instruments, and mis-operation. The sequence of events that leads to a hazardous incident can be shown as a fault tree (logic tree), such as that shown in Figure 9.6. This figure shows the set of circumstances that would result in the flooding of the chloride vaporiser shown in Figure 9.3. The AND symbol is used where coincident inputs are necessary before the system fails, and the OR symbol where failure of any input, by itself, would cause failure of the system. A fault tree is analogous to the type of logic diagram used to represent computer operations, and the symbols are analogous to logic AND and OR gates.

The fault trees for even a simple process unit will be complex, with many branches. Fault trees are used to make a quantitative assessment of the likelihood of failure of a system, using data on the reliability of the individual components of the system. For example, if the following figures represent an estimate of the probability of the events

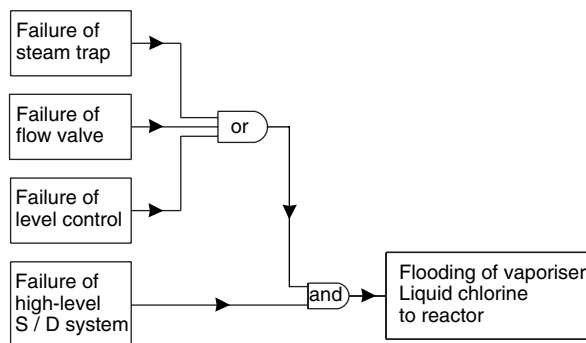


Figure 9.6. Simple fault chart (logic diagram)

shown in Figure 9.6 happening, the probability of failure of the total system by this route can be calculated.

	<i>Probability of failure</i> $\times 10^3$
Steam trap	1
Flow control valve	0.1
Level control, sub-system	0.5
High level shut-down, sub-system	0.04

The probabilities are added for OR gates, and multiplied for AND gates; so the probability of flooding the vaporiser is given by:

$$(1 + 0.1 + 0.5)10^{-3} \times 0.04 \times 10^{-3} = 0.06 \times 10^{-6}$$

The data on probabilities given in this example are for illustration only, and do not represent actual data for these components. Some quantitative data on the reliability of instruments and control systems is given by Lees (1976). Examples of the application of quantitative hazard analysis techniques in chemical plant design are given by Wells (1996) and Prugh (1980). Much of the work on the development of hazard analysis techniques, and the reliability of equipment, has been done in connection with the development of the nuclear energy programmes in the USA (USAEC, 1975) and the UK.

The Centre for Chemical Process Safety of the American Institute of Chemical Engineers has published a comprehensive and authoritative guide to quantitative risk analysis, AIChemE (2001).

Several other texts are available on the application of risk analysis techniques in the chemical process industries; see AIChemE (2000), Frank and Whittle (2001) and Kletz (1999b).

## 9.7. ACCEPTABLE RISK AND SAFETY PRIORITIES

If the consequences of an incident can be predicted quantitatively (property loss and the possible number of fatalities), then a quantitative assessment can be made of the risk.

$$\text{Quantitative assessment of risk} = \left\{ \begin{array}{l} \text{Frequency of} \\ \text{incident} \end{array} \right\} \times \left\{ \begin{array}{l} \text{loss per} \\ \text{incident} \end{array} \right\}$$

If the loss can be measured in money, the cash value of the risk can be compared with the cost of safety equipment or design changes to reduce the risk. In this way, decisions on safety can be made in the same way as other design decisions: to give the best return of the money invested.

Hazards invariably endanger life as well as property, and any attempt to make cost comparisons will be difficult and controversial. It can be argued that no risk to life should be accepted. However, resources are always limited and some way of establishing safety priorities is needed.

One approach is to compare the risks, calculated from a hazard analysis, with risks that are generally considered acceptable; such as, the average risks in the particular industry, and the kind of risks that people accept voluntarily. One measure of the risk to life is the "Fatal Accident Frequency Rate" (FAFR), defined as the number of deaths per  $10^8$  working hours. This is equivalent to the number of deaths in a group of 1000 men over their working lives. The FAFR can be calculated from statistical data for various industries and activities; some of the published values are shown in Tables 9.8 and 9.9. Table 9.8 shows the relative position of the chemical industry compared with other industries; Table 9.9 gives values for some of the risks that people accept voluntarily.

Table 9.8. FAFR for some industries for the period 1978–90

Industry	FAFR
Chemical industry	1.2
UK manufacturing	1.2
Deep sea fishing	4.2

Table 9.9. FAFR for some non-industrial activities

Activity	FAFR
Staying at home	3
Travelling by rail	5
Travelling by bus	3
Travelling by car	57
Travelling by air	240
Travelling by motor cycle	660
Rock climbing	4000

Source: Brown (2004).

In the chemical process industries it is generally accepted that risks with an FAFR greater than 0.4 (one-tenth of the average for the industry) should be eliminated as a matter of priority, the elimination of lesser risks depending on the resources available; see Kletz (1977a). This criterion is for risks to employees; for risks to the general public (undertaken involuntarily) a lower criterion must be used. The level of risk to which the public outside the factory gate should be exposed by the operations will always be a matter of debate and controversy. Kletz (1977b) suggests that a hazard can be considered acceptable if the average risk is less than one in 10 million, per person, per year. This is equivalent to a FAFR of 0.001; about the same as deaths from the bites of venomous creatures in the UK, or the chance of being struck by lightning.



For further reading on the subject of acceptable risk and risk management, see Cox and Tait (1998).

## 9.8. SAFETY CHECK LISTS

Check lists are useful aids to memory. A check list that has been drawn up by experienced engineers can be a useful guide for the less experienced. However, too great a reliance should never be put on the use of check lists, to the exclusion of all other considerations and techniques. No check list can be completely comprehensive, covering all the factors to be considered for any particular process or operation.

A short safety check list, covering the main items which should be considered in process design, is given below.

More detailed check lists are given by Carson and Mumford (1988) and Wells (1980). Balemans (1974) gives a comprehensive list of guidelines for the safe design of chemical plant, drawn up in the form of a check list. A loss prevention check list is included in the Dow Fire and Explosion Index Hazard Classification Guide, Dow (1987).

### ***Design safety check list***

#### *Materials*

- (a) flash-point
- (b) flammability range
- (c) autoignition temperature
- (d) composition
- (e) stability (shock sensitive?)
- (f) toxicity, TLV
- (g) corrosion
- (h) physical properties (unusual?)
- (i) heat of combustion/reaction

#### *Process*

1. Reactors
  - (a) exothermic —heat of reaction
  - (b) temperature control—emergency systems
  - (c) side reactions—dangerous?
  - (d) effect of contamination
  - (e) effect of unusual concentrations (including catalyst)
  - (f) corrosion
2. Pressure systems
  - (a) need?
  - (b) design to current codes (BS 5500)
  - (c) materials of construction—adequate?
  - (d) pressure relief—adequate?
  - (e) safe venting systems
  - (f) flame arresters

*Control systems*

- (a) fail safe
- (b) back-up power supplies
- (c) high/low alarms and trips on critical variables
  - (i) temperature
  - (ii) pressure
  - (iii) flow
  - (iv) level
  - (v) composition
- (d) back-up/duplicate systems on critical variables
- (e) remote operation of valves
- (f) block valves on critical lines
- (g) excess-flow valves
- (h) interlock systems to prevent mis-operation
- (i) automatic shut-down systems

*Storages*

- (a) limit quantity
- (b) inert purging/blanketing
- (c) floating roof tanks
- (d) dykeing
- (e) loading/unloading facilities — safety
- (f) earthing
- (g) ignition sources — vehicles

*General*

- (a) inert purging systems needed
- (b) compliance with electrical codes
- (c) adequate lighting
- (d) lightning protection
- (e) sewers and drains adequate, flame traps
- (f) dust-explosion hazards
- (g) build-up of dangerous impurities — purges
- (h) plant layout
  - (i) separation of units
  - (ii) access
  - (iii) siting of control rooms and offices
  - (iv) services
- (i) safety showers, eye baths

*Fire protection*

- (a) emergency water supplies
- (b) fire mains and hydrants
- (c) foam systems
- (d) sprinklers and deluge systems
- (e) insulation and protection of structures
- (f) access to buildings
- (g) fire-fighting equipment

The check list is intended to promote thought; to raise questions such as: is it needed, what are the alternatives, has provision been made for, check for, has it been provided?

## 9.9. MAJOR HAZARDS

A series of major accidents at manufacturing sites and storage installation has focused the attention of national governments on the need to control the planning and operation of sites where there is the potential for a major accident. That is, those sites posing a substantial threat to the employees, the public and the environment.

In the United Kingdom this is covered by the Control of Major Accident Hazards Regulations 1999 (COMAH), set up by the HSE (Health and Safety Executive) to implement the Seveso II directive of the EC (European Union): see [www.hse.gov.uk](http://www.hse.gov.uk). The COMAH regulations supersede the previous CIMAH (1984) regulations, set up under Seveso I.

Other countries have set up similar regulations for the control of major hazards.

The aim of the COMAH regulations is to prevent major accidents involving dangerous materials from occurring and to mitigate the effects on people and the environment.

The COMAH regulations apply to both the manufacture and storage of dangerous substances. They will, in effect, apply to any chemical manufacturing process involving flammable or toxic materials that are likely to constitute a hazard. The degree of the hazard with material storage depends on the nature of the material and the quantity stored. The regulations define the minimum storage quantities for hazardous substances above which the regulations will apply.

The regulations require industrial companies to report on the operation of dangerous installations, and on the storage of dangerous materials.

It is the duty of the company to prepare a Major Accident Prevention Policy (MAPP). This will set out the policies for ensuring the safe operation of the plant and the protection of employees and the environment. It will include details of the safety management organisation that will implement the policy.

The report should include:

- i. Identification of the hazards.
- ii. The steps taken to ensure the proper design, testing and operation of the plant.
- iii. The steps taken to prevent or minimise the consequences that would follow a major incident.
- iv. The programme for training employees and providing them with safety equipment.
- v. The preparation and procedures for updating an emergency plan covering procedures to deal with a major incident.
- vi. The procedures for informing the public living outside the site, who may be affected by a major accident, of the nature of the hazard, and what to do in the event of an accident.
- vii. Policies for liaising with the local authorities in the preparation of an off-site emergency plan.

In preparing the report for the HSE the company would usually prepare a safety case assessing the nature and degree of the hazard and the consequences of an incident. This

would include details of the measures taken to alleviate the hazard and the consequences of an accident.

The preparation of safety cases under the CIMAH regulations is covered by Lees and Ang (1989). The company is required to report any major incident to the Health and Safety Executive (HSE).

The regulations covering the control of major industrial accident hazards in the United States are discussed by Brooks *et al.* in Lees and Ang (1989). Major hazards and their management are covered by Wells (1997).

### 9.9.1. Computer software for quantitative risk analysis

The assessment of the risks and consequences involved in the planning and operation of a major plant site is a daunting task.

The methodology of the classical method of quantitative risk analysis is shown in Figure 9.7. First, the likely frequency of failure of equipment, pipe-lines, and storage vessels must be predicted; using the techniques mentioned in Section 9.6. The probable magnitude of any discharges must then be estimated, and the consequences of failure evaluated: fire, explosion or toxic fume release. Other factors, such as, site geography, weather conditions, site layout, and safety management practices, must be taken into consideration. The dispersion of gas clouds can be predicted using suitable models. This methodology enables the severity of the risks to be assessed. Limits have to be agreed on the acceptable risks; such as the permitted concentrations of toxic gases. Decisions can then be made on the siting of plant equipment (see Chapter 14), on the suitability of a site location, and on emergency planning procedures.

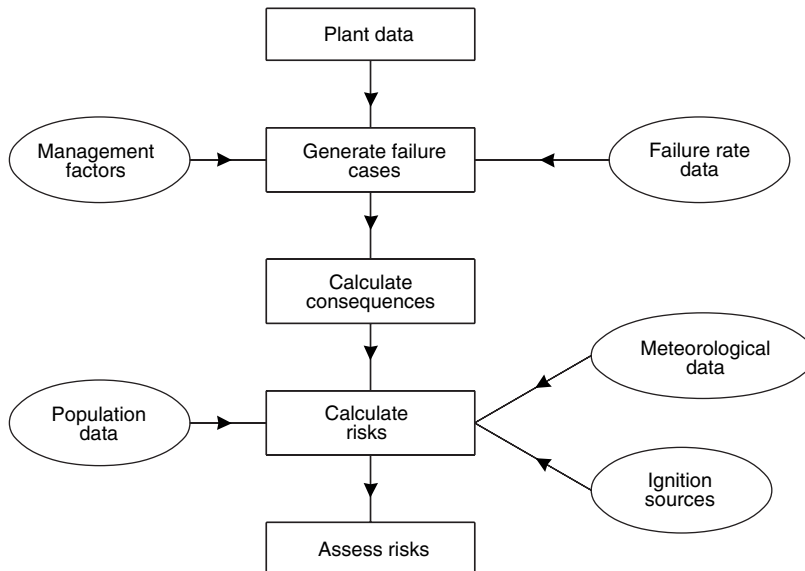


Figure 9.7. Quantitative risk assessment procedure

The comprehensive and detailed assessment of the risks required for a “safety-case” can only be satisfactorily carried out for major installations with the aid of computer software. Suites of programmes for quantitative risk analysis have been developed over the past decade by consulting firms specializing in safety and environmental protection. Typical of the software available is the SAFETI (Suite for Assessment of Flammability Explosion and Toxic Impact) suite of programs developed by DNV Technica Ltd. These programs were initially developed for the authorities in the Netherlands, as a response to the Seveso Directives of the EU (which requires the development of safety cases and hazard reviews). The programs have subsequently been developed further and extended, and are widely used in the preparation of safety cases; see Pitblado *et al.* (1990).

Computer programs can be used to investigate a range of possible scenarios for a site. But, as with all computer software used in design, they should not be used without caution and judgement. They would normally be used with the assistance and guidance of the consulting firm supplying the software. With intelligent use, guided by experience, such programs can indicate the magnitude of the likely risks at a site, and allow sound decisions to be made when licensing a process operation or granting planning permission for a new installation.

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## British Standards

- |            |         |  |
|------------|---------|--|
| BS 2915:   | 1990    | Specification for bursting discs and bursting disc devices.  |
| BS 5345:   | 1977–90 | Code of practice for the installation and maintenance of electrical apparatus for use in potentially explosive atmospheres (other than mining applications or explosives processing and manufacture), 8 parts. |
| BS 5501:   | 1977–82 | Electrical apparatus for potentially explosive atmospheres, 9 parts.   |
| BS 5908:   | 1990    | Code of practice for fire precautions in the chemical and allied industries.   |
| BS 5958:   | 1991    | Code of practice for the control of undesirable static electricity.  |
|            | Part 1: | General considerations.  |
|            | Part 2: | Recommendations for particular industries.   |
| BS 2000-34 | 2002    | Methods of test for petroleum and its products. Determination of flash point. Pensky-Martens closed cup method.  |
| BS 2000-35 | 1993    | Methods of test for petroleum and its products. Determination of open, flash and fire point. Pensky-Martens method.  |

## 9.11. PROBLEMS

- 9.1.** In the storage of flammable liquids, if the composition of the vapour–air mixture above the liquid surface falls within the flammability limits, a floating roof tank would be used or the tank blanketed with inert gas. Check if the vapour composition for liquids listed below will fall within their flammability range, at atmospheric pressure and 25°C.

1. Toluene
  2. Acrylonitrile
  3. Nitrobenzene
  4. Acetone
- 9.2.** Estimate the Dow Fire and Explosion Index, and determine the hazard rating, for the processes listed below.  
Use the process descriptions given in Appendix G and develop the designs, as needed, to estimate the index.
1. Ethylhexanol from propylene and synthesis gas, G.1.
  2. Chlorobenzenes from benzene and chlorine, G.2.
  3. Methyl ethyl ketone from 2-butanol, G.3.
  4. Acrylonitrile from propylene and ammonia, G.4.
  5. Aniline from nitrobenzene and hydrogen. G.8.
- 9.3.** Devise a preliminary control scheme for the sections of the nitric acid plant described in Chapter 4, flow-sheet Figure 4.2, which are listed below. Make a practice HAZOP study of each section and revise your preliminary control scheme.
1. Waste heat boiler (WHB)
  2. Condenser
  3. Absorption column



# *Equipment Selection, Specification and Design*

## **10.1. INTRODUCTION**

The first chapters of this book covered process design: the synthesis of the complete process as an assembly of units; each carrying out a specific process operation. In this and the following chapters, the selection, specification and design of the equipment required to carry out the function of these process units (unit operations) is considered in more detail. The equipment used in the chemical processes industries can be divided into two classes: proprietary and non-proprietary. Proprietary equipment, such as pumps, compressors, filters, centrifuges and dryers, is designed and manufactured by specialist firms. Non-proprietary equipment is designed as special, one-off, items for particular processes; for example, reactors, distillation columns and heat exchangers.

Unless employed by one of the specialist equipment manufacturers, the chemical engineer is not normally involved in the detailed design of proprietary equipment. His job will be to select and specify the equipment needed for a particular duty; consulting with the vendors to ensure that the equipment supplied is suitable. He may be involved with the vendor's designers in modifying standard equipment for particular applications; for example, a standard tunnel dryer designed to handle particulate solids may be adapted to dry synthetic fibres.

As was pointed out in Chapter 1, the use of standard equipment, whenever possible, will reduce costs.

Reactors, columns and other vessels are usually designed as special items for a given project. In particular, reactor designs are usually unique, except where more or less standard equipment is used; such as an agitated, jacketed, vessel.

Distillation columns, vessels and tubular heat exchangers, though non-proprietary items, will be designed to conform to recognised standards and codes; this reduces the amount of design work involved.

The chemical engineer's part in the design of "non-proprietary" equipment is usually limited to selecting and "sizing" the equipment. For example, in the design of a distillation column his work will typically be to determine the number of plates; the type and design of plate; diameter of the column; and the position of the inlet, outlet and instrument nozzles. This information would then be transmitted, in the form of sketches and specification sheets, to the specialist mechanical design group, or the fabricator's design team, for detailed design.

In this chapter the emphasis is put on equipment selection, rather than equipment design; as most of the equipment described is proprietary equipment. Design methods

are given for some miscellaneous non-proprietary items. A brief discussion of reactor design is included. The design of two important classes of equipment, columns and heat exchangers, is covered separately in Chapters 11 and 12. A great variety of equipment is used in the process industries, and it is only possible to give very brief descriptions of the main types in this volume. Further details are given in Volume 2; and descriptions and illustrations of most of the equipment used can be found in various handbooks: Perry *et al.* (1997), Schweitzer (1988) and Walas (1990). Equipment manufacturers' advertisements in the technical press should also be studied. It is worthwhile building up a personal file of vendors' catalogues to supplement those that may be held in a firm's library. In the United Kingdom, a commercial organisation, Technical Indexes Ltd., publishes the Process Engineering Index; which contains on microfilm information from over 3000 manufacturers and suppliers of process equipment.

The scientific principles and theory that underlie the design of and operation of processing equipment is covered in Volume 2.

## 10.2. SEPARATION PROCESSES

As was discussed in Chapter 1, chemical processes consist essentially of reaction stages followed by separation stages in which the products are separated and purified.

The main techniques used to separate phases, and the components within phases, are listed in Table 10.1 and discussed in Sections 10.3 to 10.9.

## 10.3. SOLID-SOLID SEPARATIONS

Processes and equipment are required to separate valuable solids from unwanted material, and for size grading (classifying) solid raw materials and products.

The equipment used for solid-solid separation processes was developed primarily for the minerals processing and metallurgical industries for the beneficiation (up-grading) of ores. The techniques used depend on differences in physical, rather than chemical, properties, though chemical additives may be used to enhance separation. The principal techniques used are shown in Figure 10.1; which can be used to select the type of processes likely to be suitable for a particular material and size range.

Sorting material by appearance, by hand, is now rarely used due to the high cost of labour.

### 10.3.1. Screening (sieving)

The methods used for laboratory particle size analysis are discussed in detail in Volume 2, Chapter 1.

Screens separate particles on the basis of size. Their main application is in grading raw materials and products into size ranges, but they are also used for the removal of trash (over- and under-sized contaminants) and for dewatering. Industrial screening equipment is used over a wide range of particle sizes, from fine powders to large rocks. For small particles woven cloth or wire screens are used, and for larger sizes, perforated metal plates or grids.

Table 10.1. Separation processes

Numbers refer to the sections in this chapter. Processes in brackets are used for separating dissolved components (solutions). The terms major and minor component only apply where different phases are to be separated; i.e. not to those on the diagonal

		MINOR COMPONENT					
		SOLID		LIQUID		GAS/VAPOUR	
MAJOR COMPONENT	SOLID	Sorting 10.3 Screening 10.3.1 Hydrocyclones 10.3.2 Classifiers 10.3.3 Jigs 10.3.4 Tables 10.3.5 Centrifuges 10.3.6 Dense media 10.3.7 Flotation 10.3.8 Magnetic 10.3.9 Electrostatic 10.3.10	Pressing 10.4.5 Drying 10.4.6.	Crushing 10.10 Heating —			
	LIQUID	Thickeners 10.4.1 Clarifiers 10.4.1 Hydrocyclones 10.4.4 Filtration 10.4.2 Centrifuges 10.4.3 (Crystallisers) 10.5.2 (Evaporators) 10.5.1	Decanters 10.6.1 Coalescers 10.6.3 (Solvent extraction) 10.7.1 (Distillation) Chapter 11 (Adsorption) Volume 2 (Ion exchange) Volume 2	(Stripping) Volume 2			
	GAS/VAPOUR	Gravity settlers 10.8.1 Impingement settlers 10.8.2 Cyclones 10.8.3 Filters 10.8.4 Wet scrubbers 10.8.5 Electrostatic precipitators 10.8.6	Separating vessels 10.9 Demisting pads 10.9 Cyclones 10.8.3 Wet scrubbers 10.8.5 Electrostatic precipitators 10.8.6	(Adsorption) Volume 2 (Absorption) Volume 2			

Screen sizes are defined in two ways: by a mesh size number for small sizes and by the actual size of opening in the screen for the larger sizes. There are several different standards in use for mesh size, and it is important to quote the particular standard used when specifying particle size ranges by mesh size. In the UK the appropriate British Standards should be used; BS 410 and BS 1796. A comparison of the various international standard sieve mesh sizes is given in Volume 2, Chapter 1.

The simplest industrial screening equipment are stationary screens, over which the material to be screened flows. Typical of this type are “Grizzly” screens, which consist of rows of equally spaced parallel bars, and which are used to “scalp” off over-sized rocks in the feed to crushers.

Dynamic screening equipment can be categorised according to the type of motion used to shake-up and transport the material on the screen. The principal types used in the chemical process industries are described briefly below.

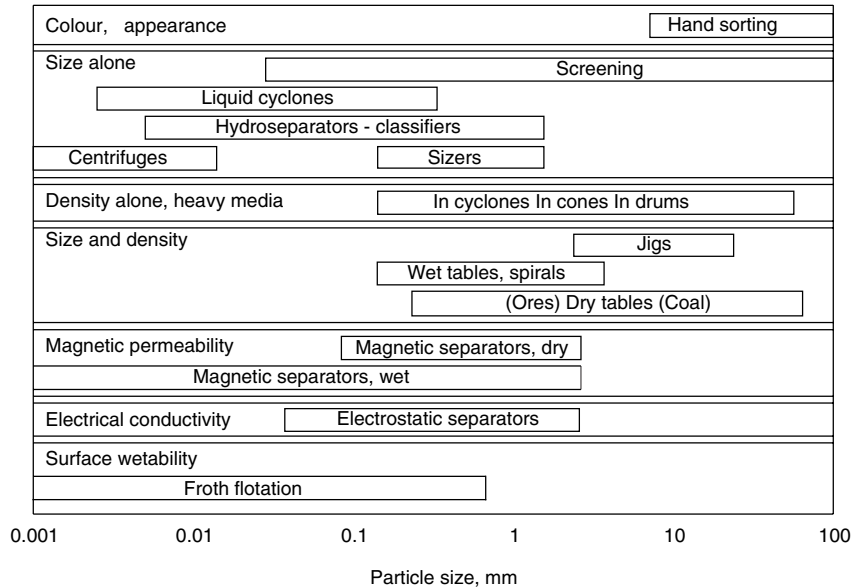


Figure 10.1. A particle size selection guide to solid-solid separation techniques and equipment (after Roberts *et al.* 1971)

*Vibrating screens:* horizontal and inclined screening surfaces vibrated at high frequencies (1000 to 7000 Hz). High capacity units, with good separating efficiency, which are used for a wide range of particle sizes.

*Oscillating screens:* operated at lower frequencies than vibrating screens (100–400 Hz) with a longer, more linear, stroke.

*Reciprocating screens:* operated with a shaking motion, a long stroke at low frequency (20–200 Hz). Used for conveying with size separation.

*Shifting screens:* operated with a circular motion in the plane of the screening surface. The actual motion may be circular, gyratory, or circularly vibrated. Used for the wet and dry screening of fine powders.

*Revolving screens:* inclined, cylindrical screens, rotated at low speeds (10–20 rpm). Used for the wet screening of relatively coarse material, but have now been largely replaced by vibrating screens.

Figure 10.2, which is based on a similar chart given by Matthews (1971), can be used to select the type of screening equipment likely to be suitable for a particular size range. Equipment selection will normally be based on laboratory and pilot scale screening tests, conducted with the co-operation of the equipment vendors. The main factors to be considered, and the information that would be required by the firms supplying proprietary screening equipment, are listed below:

1. Rate, throughput required.
2. Size range (test screen analysis).
3. Characteristics of the material: free-flowing or sticky, bulk density, abrasiveness.
4. Hazards: flammability, toxicity, dust explosion.
5. Wet or dry screening to be used.

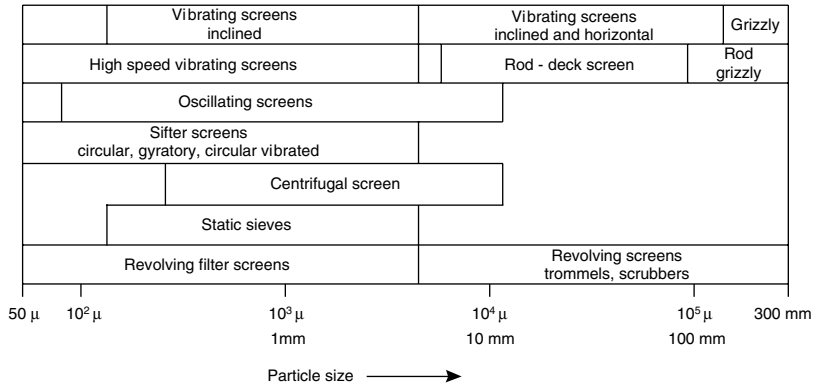


Figure 10.2. Screen selection by particle size range

### 10.3.2. Liquid-solid cyclones

Cyclones can be used for the classification of solids, as well as for liquid-solid, and liquid-liquid separations. The design and application of liquid cyclones (hydrocyclones) is discussed in Section 10.4.4. A typical unit is shown in Figure 10.3.

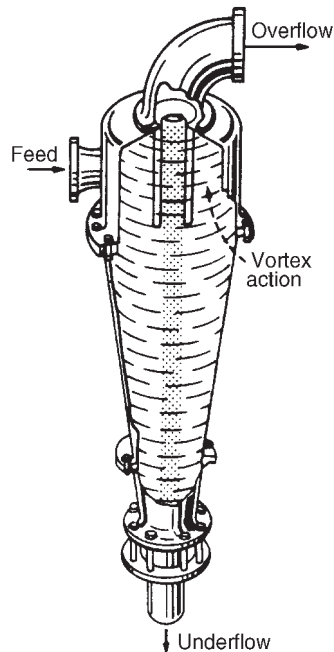


Figure 10.3. Liquid-solid cyclone (hydrocyclone)

Liquid cyclones can be used for the classification of solid particles over a size range from 5 to 100  $\mu\text{m}$ . Commercial units are available in a wide range of materials of

construction and sizes; from as small as 10 mm to up to 30 m diameter. The separating efficiency of liquid cyclones depends on the particle size and density, and the density and viscosity of the liquid medium.

### 10.3.3. Hydroseparators and sizers (classifiers)

Classifiers that depend on the difference in the settling rates of different size particles in water are frequently used for separating fine particles, in the 50 to 300  $\mu\text{m}$  range. Various designs are used. The principal ones used in the chemical process industries are described below.

*Thickeners:* thickeners are primarily used for liquid-solid separation (see Section 10.4). When used for classification, the feed rate is such that the overflow rate is greater than the settling rate of the slurry, and the finer particles remain in the overflow stream.

*Rake classifiers:* are inclined, shallow, rectangular troughs, fitted with mechanical rakes at the bottom to rake the deposited solids to the top of the incline (Figure 10.4). Several rake classifiers can be used in series to separate the feed into different size ranges.

*Bowl classifiers:* are shallow bowls with concave bottoms, fitted with rakes. Their operation is similar to that of thickeners.

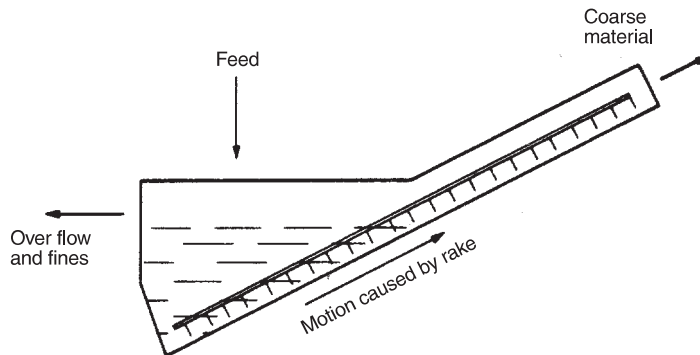


Figure 10.4. Rake classifier

### 10.3.4. Hydraulic jigs

Jigs separate solids by difference in density and size. The material is immersed in water, supported on a screen (Figure 10.5). Pulses of water are forced through the bed of material, either by moving the screen or by pulsating the water level. The flow of water fluidises the bed and causes the solids to stratify with the lighter material at the top and the heavier at the bottom.

### 10.3.5. Tables

Tables are used wet and dry. The separating action of a wet table resembles that of the traditional miner's pan. Riffled tables (Figure 10.6) are basically rectangular decks, inclined at a shallow angle to the horizontal (2 to 5°), with shallow slats (riffles) fitted to

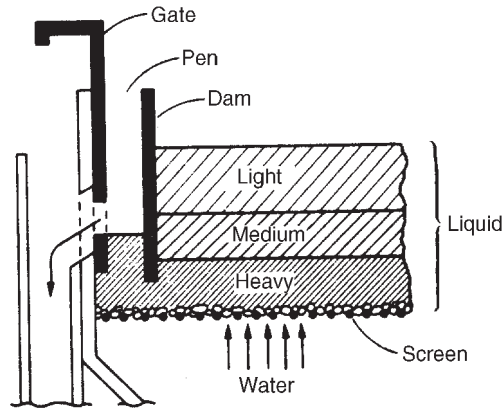


Figure 10.5. A hydraulic jig

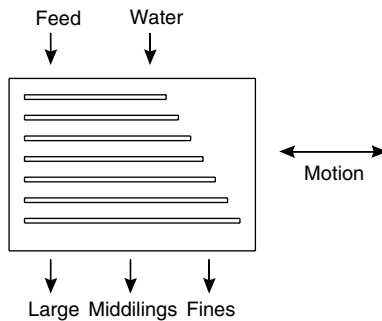


Figure 10.6. Wilfley riffled table

the surface. The table is mechanically shaken, with a slow stroke in the forward direction and a faster backward stroke. The particles are separated into different size ranges under the combined action of the vibration, water flow, and the resistance to flow over the riffles.

### 10.3.6. Classifying centrifuges

Centrifuges are used for the classification of particles in size ranges below  $10 \mu\text{m}$ . Two types are used: solid bowl centrifuges, usually with a cylindrical, conical bowl, rotated about a horizontal axis; and “nozzle” bowl machines, fitted with discs.

These types are described in Section 10.4.3.

### 10.3.7. Dense-medium separators (sink and float processes)

Solids of different densities can be separated by immersing them in a fluid of intermediate density. The heavier solids sink to the bottom and the lighter float to the surface. Water suspensions of fine particles are often used as the dense liquid (heavy-medium). The technique is used extensively for the beneficiation (concentration) of mineral ores.

### 10.3.8. Flotation separators (froth-flotation)

Froth-flotation processes are used extensively for the separation of finely divided solids. Separation depends on differences in the surface properties of the materials. The particles are suspended in an aerated liquid (usually water), and air bubbles adhere preferentially to the particles of one component and bring them to the surface. Frothing agents are used so that the separated material is held on the surface as a froth and can be removed.

Froth-flotation is an extensively used separation technique, having a wide range of applications in the minerals processing industries and other industries. It can be used for particles in the size range from 50 to 400  $\mu\text{m}$ .

### 10.3.9. Magnetic separators

Magnetic separators can be used for materials that are affected by magnetic fields; the principle is illustrated in Figure 10.7. Rotating-drum magnetic separators are used for a wide range of materials in the minerals processing industries. They can be designed to handle relatively high throughputs, up to 3000 kg/h per metre length of drum.

Simple magnetic separators are often used for the removal of iron from the feed to a crusher.

The various types of magnetic separators used and their applications are described by Bronkala (1988).

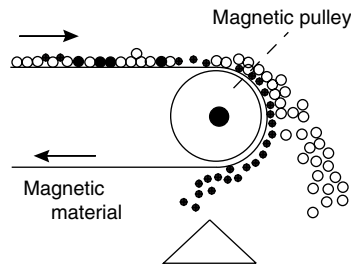


Figure 10.7. Magnetic separator

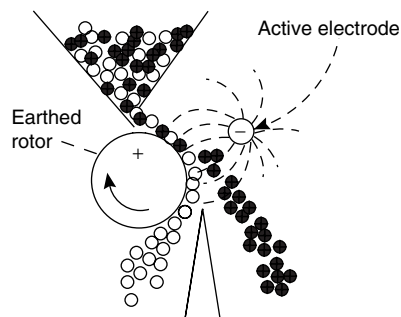


Figure 10.8. Electrostatic separator



### 10.3.10. Electrostatic separators

Electrostatic separation depends on differences in the electrical properties (conductivity) of the materials to be treated. In a typical process the material particles pass through a high-voltage electric field as it is fed on to a revolving drum, which is at earth potential (Figure 10.8). Those particles that acquire a charge adhere to the drum surface and are carried further around the drum before being discharged.

## 10.4. LIQUID-SOLID (SOLID-LIQUID) SEPARATORS

The need to separate solid and liquid phases is probably the most common phase separation requirement in the process industries, and a variety of techniques is used (Figure 10.9). Separation is effected by either the difference in density between the liquid and solids, using either gravity or centrifugal force, or, for filtration, depends on the particle size and shape. The most suitable technique to use will depend on the solids concentration and feed rate, as well as the size and nature of the solid particles. The range of application of various techniques and equipment, as a function of slurry concentration and particle size, is shown in Figure 10.10.

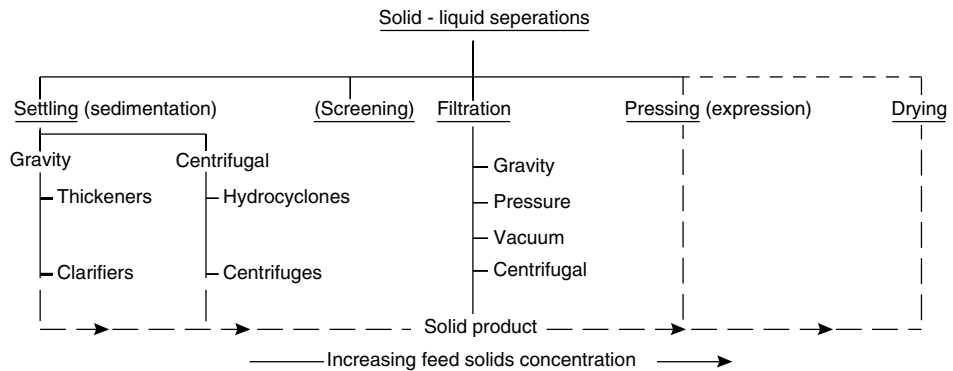


Figure 10.9. Solid-liquid separation techniques

The choice of equipment will also depend on whether the prime objective is to obtain a clear liquid or a solid product, and on the degree of dryness of the solid required.

The design, construction and application of thickeners, centrifuges and filters is a specialised subject, and firms who have expertise in these fields should be consulted when selecting and specifying equipment for new applications. Several specialist texts on the subject are available: Svarovsky (2001), Ward (2000) and Wakeman and Tarleton (1998). The theory of sedimentation processes is covered in Volume 2, Chapter 5 and filtration in Chapter 7.

### 10.4.1. Thickeners and clarifiers

Thickening and clarification are sedimentation processes, and the equipment used for the two techniques are similar. The primary purpose of thickening is to increase the concentration of a relatively large quantity of suspended solids; whereas that of clarifying,

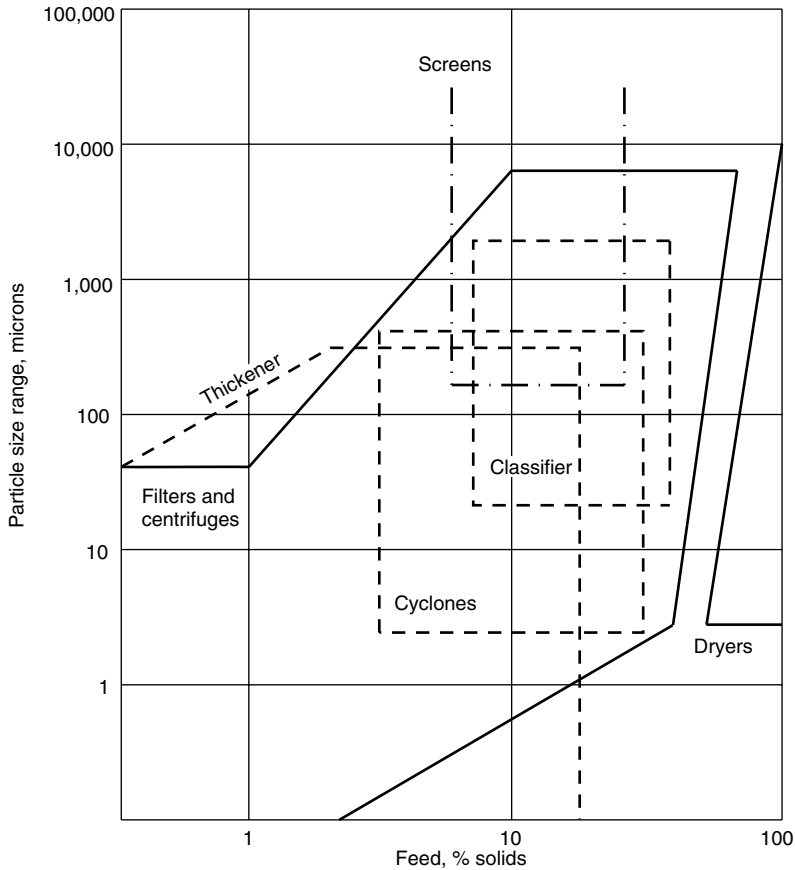


Figure 10.10. Solid-liquid separation techniques (after Dahlstrom and Cornell, 1971)

as the name implies, is to remove a small quantity of fine solids to produce a clear liquid effluent. Thickening and clarification are relatively cheap processes when used for the treatment of large volumes of liquid.

A thickener, or clarifier, consists essentially of a large circular tank with a rotating rake at the base. Rectangular tanks are also used, but the circular design is preferred. They can be classified according to the way the rake is supported and driven. The three basic designs are shown in Figure 10.11 (see p. 410). Various designs of rake are used, depending on the nature of the solids.

The design and construction of thickeners and clarifiers is described by Dahlstrom and Cornell (1971).

Flocculating agents are often added to promote the separating performance of thickeners.

#### 10.4.2. Filtration

In filtration processes the solids are separated from the liquid by passing (filtering) the slurry through some form of porous filter medium. Filtration is a widely used separation

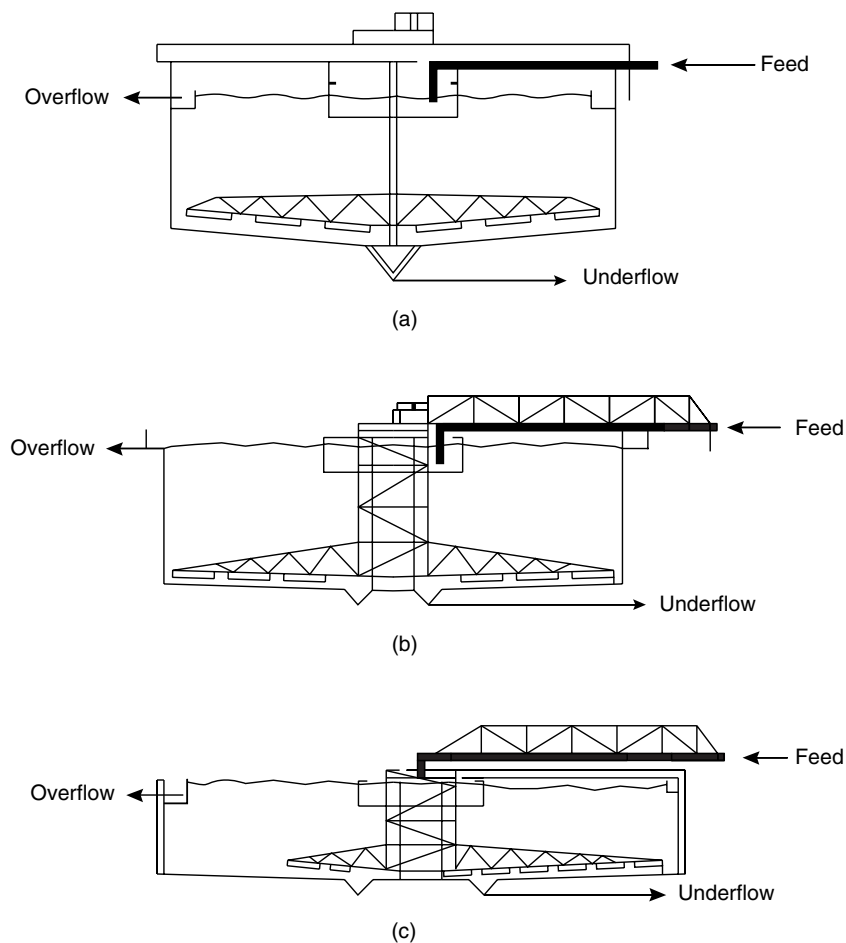


Figure 10.11. Types of thickener and clarifier (a) Bridge supported (up to <math><40\text{ m}</math> dia.) (b) Centre column supported (<math><30\text{ m}</math> dia.) (c) Traction driven (<math><60\text{ m}</math> dia.)

process in the chemical and other process industries. Many types of equipment and filter media are used; designed to meet the needs of particular applications. Descriptions of the filtration equipment used in the process industries and their fields of application can be found in various handbooks: Perry *et al.* (1997), Dickenson (1997), Schweitzer (1997), and in several specialist texts on the subject: Cheremisinoff (1998), Orr (1977). A short discussion of filtration theory and descriptions of the principal types of equipment is given in Volume 2, Chapter 7.

The most commonly used filter medium is woven cloth, but a great variety of other media is also used. The main types are listed in Table 10.2. A comprehensive discussion of the factors to be considered when selecting filter media is given by Purchas (1971) and Mais (1971); see also Purchas and Sutherland (2001). Filter aids are often used to increase the rate of filtration of difficult slurries. They are either applied as a precoat

to the filter cloth or added to the slurry, and deposited with the solids, assisting in the formation of a porous cake.

Table 10.2. Filter media

Type	Examples	Minimum size particle trapped ( $\mu\text{m}$ )
1. Solid fabrications	Scalloped washers Wire-wound tubes	5
2. Rigid porous media	Ceramics, stoneware Sintered metal	1 3
3. Metal	Perforated sheets Woven wire	100 5
4. Porous plastics	Pads, sheets Membranes	3 0.005
5. Woven fabrics	Natural and synthetic fibre cloths	10
6. Non-woven sheets	Felts, lap Paper, cellulose	10 5
7. Cartridges	Yarn-wound spools, graded fibres	2
8. Loose solids	Fibres, asbestos, cellulose	sub-micron

Industrial filters use vacuum, pressure, or centrifugal force to drive the liquid (filtrate) through the deposited cake of solids. Filtration is essentially a discontinuous process. With batch filters, such as plate and frame presses, the equipment has to be shut down to discharge the cake; and even with those filters designed for continuous operation, such as rotating-drum filters, periodic stoppages are necessary to change the filter cloths. Batch filters can be coupled to continuous plant by using several units in parallel, or by providing buffer storage capacity for the feed and product.

The principal factors to be considered when selecting filtration equipment are:

1. The nature of the slurry and the cake formed.
2. The solids concentration in the feed.
3. The throughput required.
4. The nature and physical properties of the liquid: viscosity, flammability, toxicity, corrosiveness.
5. Whether cake washing is required.
6. The cake dryness required.
7. Whether contamination of the solid by a filter aid is acceptable.
8. Whether the valuable product is the solid or the liquid, or both.

The overriding factor will be the filtration characteristics of the slurry; whether it is fast filtering (low specific cake resistance) or slow filtering (high specific cake resistance). The filtration characteristics can be determined by laboratory or pilot plant tests. A guide to filter selection by the slurry characteristics is given in Table 10.3; which is based on a similar selection chart given by Porter *et al.* (1971).



removed either mechanically or by sluicing it off with jets of water. Leaf filters are used for similar applications as plate and frame presses, but generally have lower operating costs.

### **Rotary drum filters (usually vacuum operation) (Figure 10.13)**

A drum filter consists essentially of a large hollow drum round which the filter medium is fitted. The drum is partially submerged in a trough of slurry, and the filtrate sucked through the filter medium by vacuum inside the drum. Wash water can be sprayed on to the drum surface and multicompartment drums are used so that the wash water can be kept separate from the filtrate. A variety of methods is used to remove the cake from the drum: knives, strings, air jets and wires. Rotating drum filters are essentially continuous in operation. They can handle large throughputs, and are widely used for free filtering slurries.

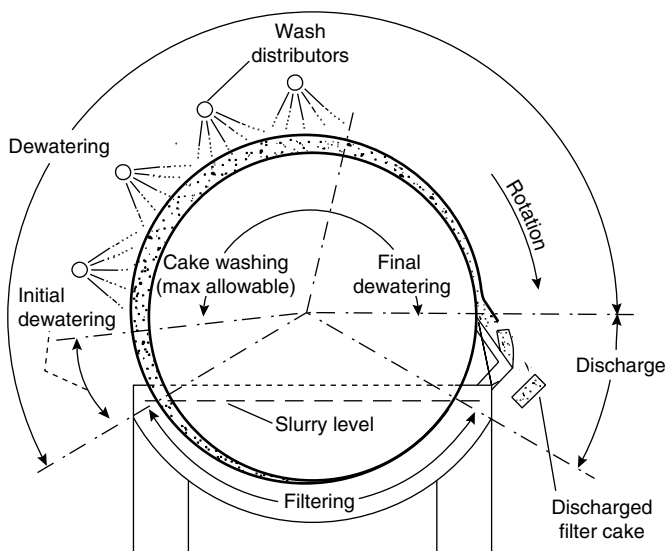


Figure 10.13. Drum filter

### **Disc filters (pressure and vacuum operation)**

Disc filters are similar in principle to rotary filters, but consist of several thin discs mounted on a shaft, in place of the drum. This gives a larger effective filtering area on a given floor area, and vacuum disc filters are used in preference to drum filters where space is restricted. At sizes above approximately 25 m<sup>2</sup> filtration area, disc filters are cheaper; but their applications are more restricted, as they are not as suitable for the application of wash water, or precoating.

### **Belt filters (vacuum operation) (Figure 10.14)**

A belt filter consists of an endless reinforced rubber belt, with drainage hole along its centre, which supports the filter medium. The belt passes over a stationary suction box, into which the filtrate is sucked. Slurry and wash water are sprayed on to the top of the belt.

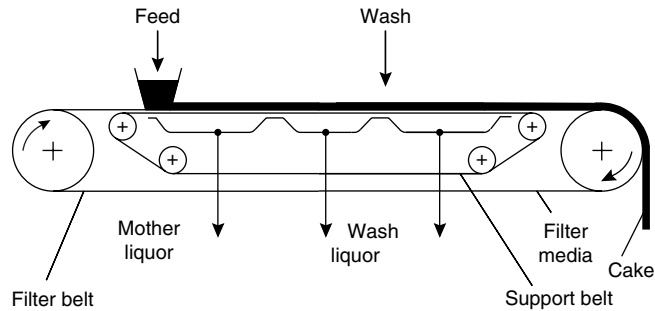


Figure 10.14. Belt filter

### ***Horizontal pan filters (vacuum operation) (Figure 10.15)***

This type is similar in operation to a vacuum Nutsche filter. It consists of shallow pans with perforated bases, which support the filter medium. By arranging a series of pans around the circumference of a rotating wheel, the operation of filtering, washing, drying and discharging can be made automatic.

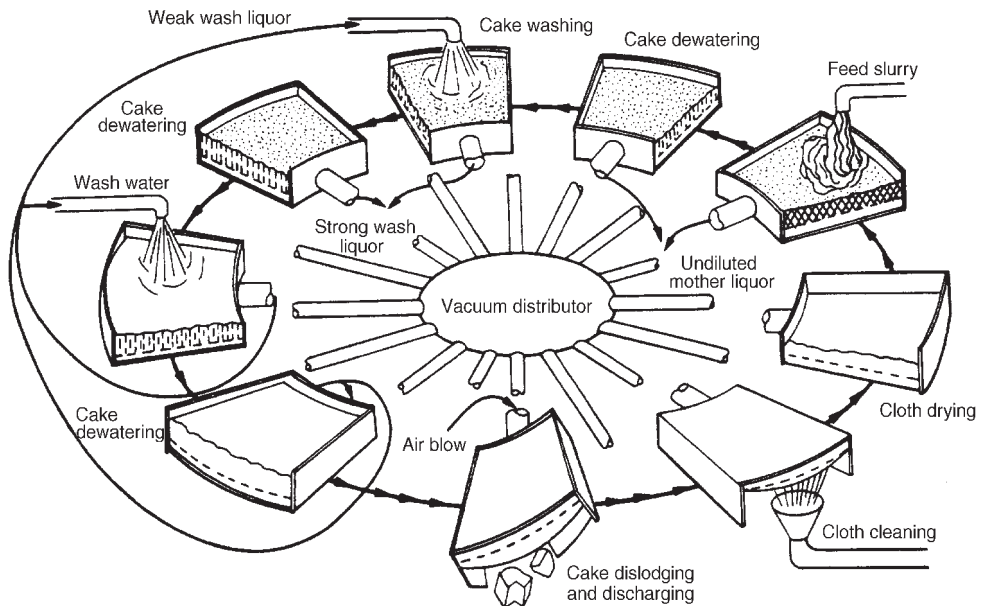


Figure 10.15. Pan filters

### ***Centrifugal filters***

Centrifugal filters use centrifugal force to drive the filtrate through the filter cake. The equipment used is described in the next section.

### 10.4.3. Centrifuges

Centrifuges are classified according to the mechanism used for solids separation:

- (a) Sedimentation centrifuges: in which the separation is dependent on a difference in density between the solid and liquid phases (solid heavier).
- (b) Filtration centrifuges: which separate the phases by filtration. The walls of the centrifuge basket are porous, and the liquid filters through the deposited cake of solids and is removed.

The choice between a sedimentation or filtration centrifuge for a particular application will depend on the nature of the feed and the product requirements.

The main factors to be considered are summarised in Table 10.4. As a general rule, sedimentation centrifuges are used when it is required to produce a clarified liquid, and filtration centrifuges to produce a pure, dry, solid.

Table 10.4. Selection of sedimentation or filter centrifuge

Factor	Sedimentation	Filtration
Solids size, fine		x
Solids size, >150 $\mu\text{m}$	x	
Compressible cakes	x	
Open cakes		x
Dry cake required		x
High filtrate clarity	x	
Crystal breakage problems		x
Pressure operation		
High-temperature operation	will depend on the type of centrifuge used	

A variety of centrifugal filter and sedimenter designs is used. The main types are listed in Table 10.5. They can be classified by a number of design and operating features, such as:

1. Mode of operation—batch or continuous.
2. Orientation of the bowl/basket—horizontal or vertical.
3. Position of the suspension and drive—overhung or underhung.
4. Type of bowl—solid, perforated basket, disc bowl.
5. Method of solids cake removal.
6. Method of liquid removal.

Descriptions of the various types of centrifuges and their fields of application can be found in various handbooks, in a book by Leung (1998) and articles by Ambler (1971) and Linley (1984).

The fields of application of each type, classified by the size range of the solid particles separated, are given in Figure 10.16. A similar selection chart is given by Schroeder (1998).

#### ***Sedimentation centrifuges***

There are four main types of sedimentation centrifuge:



Table 10.5. Centrifuge types (after Sutherland, 1970)

Sedimentation	Filtration-fixed bed
Laboratory	Vertical basket
Bottle	Manual discharge
Ultra	Bag discharge
Tubular bowl	Knife discharge
	Horizontal basket
	Inclined basket
Disc	
Batch bowl	
Nozzle discharge	
Valve discharge	
Opening bowl	
Imperforate basket	
Manual discharge	
Skimmer discharge	
Scroll discharge	
Horizontal	
Cantilevered	
Vertical	
Screen bowl	
	Filtration-moving bed
	Conical bowl
	Wide angle
	Vibrating
	Torsional
	Tumbling
	Scroll discharge
	Cylindrical bowl
	Scroll discharge
	Pusher

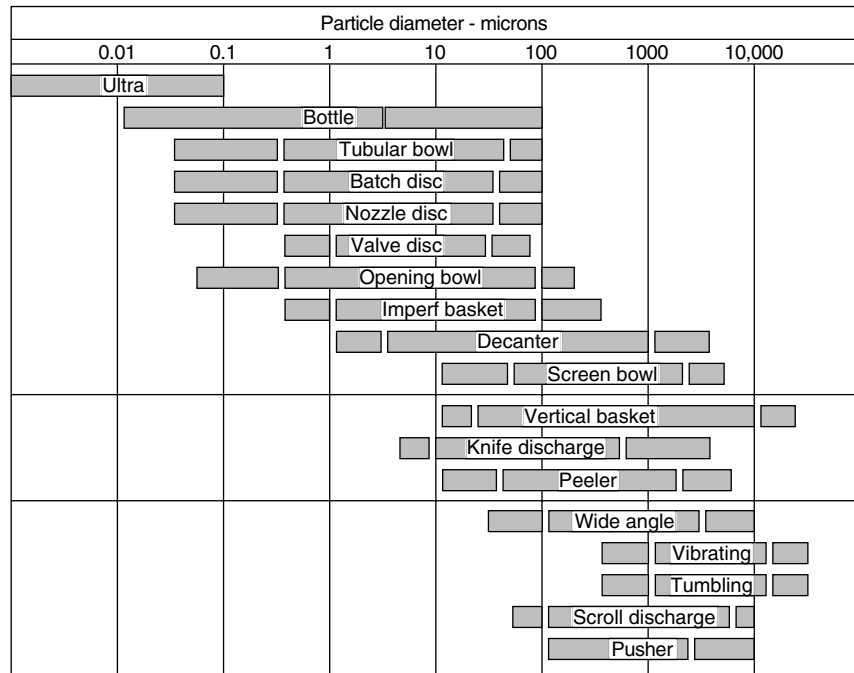


Figure 10.16. Classification of centrifuges by particle size (after Sutherland, 1970)

### 1. Tubular bowl (Figure 10.17)

High-speed, vertical axis, tubular bowl centrifuges are used for the separation of immiscible liquids, such as water and oil, and for the separation of fine solids. The bowl is driven at speeds of around 15,000 rpm (250 Hz) and the centrifugal force generated exceeds 130,000 N.

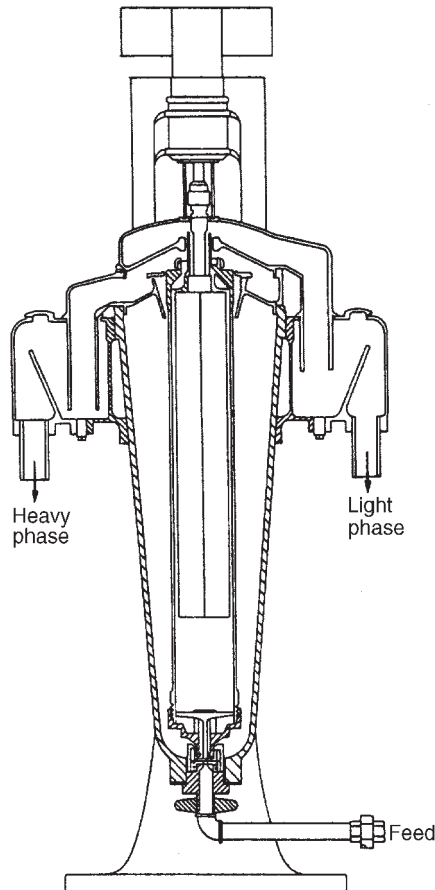


Figure 10.17. Tubular Bowl centrifuge

### 2. Disc bowl (Figure 10.18)

The conical discs in a disc bowl centrifuge split the liquid flow into a number of very thin layers, which greatly increases the separating efficiency. Disc bowl centrifuges are used for separating liquids and fine solids, and for solids classification.

### 3. Scroll discharge

In this type of machine the solids deposited on the wall of the bowl are removed by a scroll (a helical screw conveyer) which revolves at a slightly different speed from the

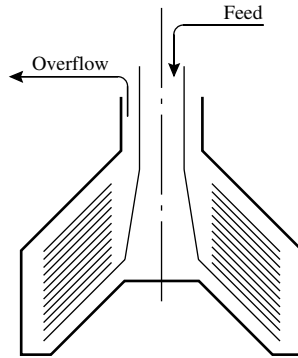


Figure 10.18. Disc bowl centrifuge

bowl. Scroll discharge centrifuges can be designed so that solids can be washed and relatively dry solids be discharged.

#### 4. Solid bowl batch centrifuge

The simplest type; similar to the tubular bowl machine type but with a smaller bowl length to diameter ratio (less than 0.75). The tubular bowl type is rarely used for solids concentrations above 1 per cent by volume. For concentrations between 1 to 15 per cent, any of the other three types can be used. Above 15 per cent, either the scroll discharge type or the batch type may be used, depending on whether continuous or intermittent operation is required.

#### **Sigma theory for sedimentation centrifuges**

The basic equations describing sedimentation in a centrifugal field have been developed in Volume 2, Chapter 9. In that discussion the term *sigma* ( $\Sigma$ ) is introduced, which can be used to define the performance of a centrifuge independently of the physical properties of the solid-fluid system. The sigma value of a centrifuge, normally expressed in  $\text{cm}^2$ , is equal to the cross-sectional area of a gravity settling tank having the same clarifying capacity.

This approach to describing centrifuge performance has become known as the “sigma theory”. It provides a means for comparing the performance of sedimentation centrifuges and for scaling up from laboratory and pilot scale tests; see Ambler (1952) and Trowbridge (1962).

In the general case, it can be shown that:

$$Q = 2u_g \Sigma \quad (10.1)$$

and (where Stokes' law applies) 
$$u_g = \frac{\Delta \rho d_s^2 g}{18\mu} \quad (10.2)$$

*Note:* The factor of 2 is included in equation 10.1 as  $d_s$  is the *cut-off* size, 50 per cent of particles of this size will be removed in passage through the centrifuge.

- where  $Q$  = volumetric flow of liquid through the centrifuge,  $\text{m}^3/\text{s}$ ,  
 $u_g$  = terminal velocity of the solid particle settling under gravity through the liquid,  $\text{m/s}$ ,  
 $\Sigma$  = sigma value of the centrifuge,  $\text{m}^2$ ,  
 $\Delta\rho$  = density difference between solid and liquid,  $\text{kg/m}^3$   
 $d_s$  = the diameter of the solid particle, *the cut-off size*,  $\text{m}$  ( $\mu\text{m} \times 10^{-6}$ ),  
 $\mu$  = viscosity of the liquid,  $\text{Nm}^{-2}\text{s}$ .  
 $g$  = gravitational acceleration,  $9.81 \text{ m/s}^2$ ,

Morris (1966) gives a method for the selection of the appropriate type of sedimentation centrifuge for a particular application based on the ratio of the liquid overflow to sigma value ( $Q/\Sigma$ ). His values for the operating range of each type, and their approximate efficiency rating, are given in Table 10.6. The efficiency term is used to account for the different amounts by which the various designs differ from the theoretical sigma values given by equation 10.1. Sigma values depend solely on the geometrical configuration and speed of the centrifuge. Details of the calculation for various types are given by Ambler (1952). To use Table 10.6, it is necessary to know the feed rate of slurry (and hence the liquid overflow  $Q$ ), the density of the liquid and solid, the liquid viscosity; and the diameter of the particle for, say, a 98 per cent size removal. The use of Table 10.6 is illustrated in Example 10.1.

Table 10.6. Selection of sedimentation centrifuges

Type	Approximate efficiency (%)	Normal operating range $Q$ , $\text{m}^3/\text{h}$ at $Q/\Sigma$ $\text{m/s}$
Tubular bowl	90	0.4 at $5 \times 10^{-8}$ to 4 at $3.5 \times 10^{-7}$
Disc	45	0.1 at $7 \times 10^{-8}$ to 110 at $4.5 \times 10^{-7}$
Solid bowl (scroll discharge)	60	0.7 at $1.5 \times 10^{-6}$ to 15 at $1.5 \times 10^{-5}$
Solid bowl (basket)	75	0.4 at $5 \times 10^{-6}$ to 4 at $1.5 \times 10^{-4}$

A selection guide for sedimentation centrifuges by Lavanchy *et al.* (1964), which includes other types of solid-liquid separators, is shown in Figure 10.19, adapted to SI units.

### Example 10.1

A precipitate is to be continuously separated from a slurry. The solids concentration is 5 per cent and the slurry feed rate  $5.5 \text{ m}^3/\text{h}$ . The relevant physical properties at the system operating temperature are:

liquid density  $1050 \text{ kg/m}^3$ , viscosity  $4 \text{ cp}$  ( $\text{mNm}^{-2}\text{s}$ ),

solid density  $2300 \text{ kg/m}^3$ , “cut-off” particle size  $10 \mu\text{m} = 10 \times 10^{-6} \text{ m}$ .

### Solution

$$\begin{aligned} \text{Overflow rate, } Q &= 0.95 \times 5.5 = 5.23 \text{ m}^3/\text{h} \\ &= \frac{5.13}{3600} = 1.45 \times 10^{-3} \text{ m}^3/\text{s} \\ \Delta\rho &= 2300 - 1050 = 1250 \text{ kg/m}^3 \end{aligned}$$

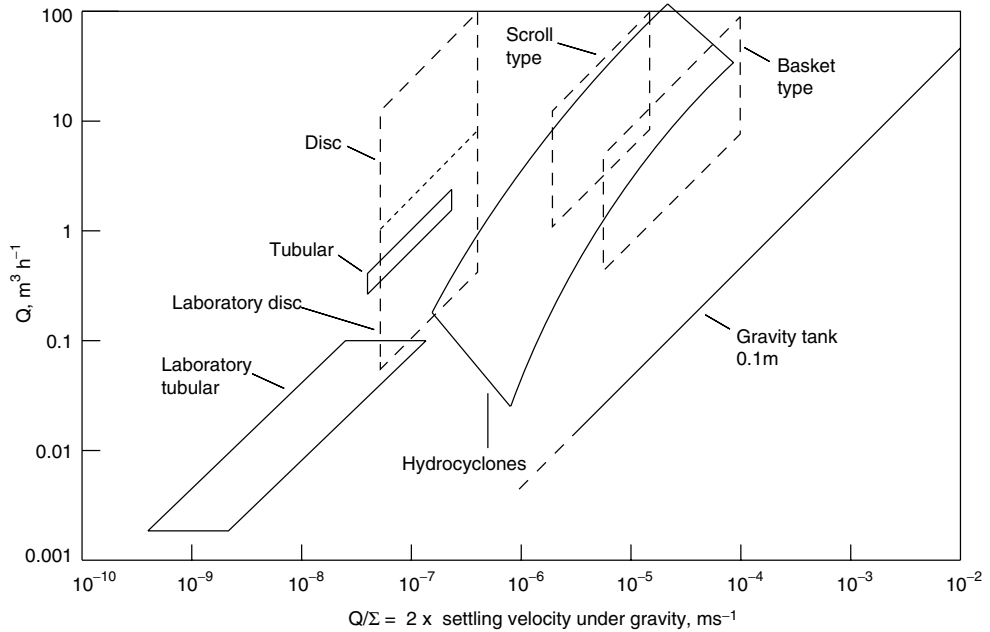


Figure 10.19. Performance of sedimentation equipment (after Lavanchy *et al.*, 1964)

From equations 10.1 and 10.2

$$\frac{Q}{\Sigma} = 2 \times \frac{1250(10 \times 10^{-6})^2}{18 \times 4 \times 10^{-3}} \times 9.81 = 3.4 \times 10^{-5}$$

From Table 10.6 for a  $Q$  of  $5.23 \text{ m}^3/\text{h}$  at a  $Q/\Sigma$  of  $3.4 \times 10^{-5}$  a solid bowl basket type should be used.

To obtain an idea of the size of the machine needed the sigma value can be calculated using the efficiency value from Table 10.6.

From equation 10.1:

$$\begin{aligned} \Sigma &= \frac{Q}{\text{eff.} \times 2u_g} = \frac{1.45 \times 10^{-3}}{0.75 \times 3.4 \times 10^{-5}} \\ &= \underline{\underline{56.9 \text{ m}^2}} \end{aligned}$$

The sigma value is the equivalent area of a gravity settler that would perform the same separation as the centrifuge.

### **Filtration centrifuges (centrifugal filters)**

It is convenient to classify centrifugal filters into two broad classes, depending on how the solids are removed: fixed bed or moving bed.

In the fixed-bed type, the cake of solids remains on the walls of the bowl until removed manually, or automatically by means of a knife mechanism. It is essentially cyclic in operation. In the moving-bed type, the mass of solids is moved along the bowl by the

action of a scroll (similar to the solid-bowl sedimentation type); or by a ram (pusher type); or by a vibration mechanism; or by the bowl angle. Washing and drying zones can be incorporated into the moving bed type.

Bradley (1965) has grouped the various types into the family tree shown in Figure 10.20.

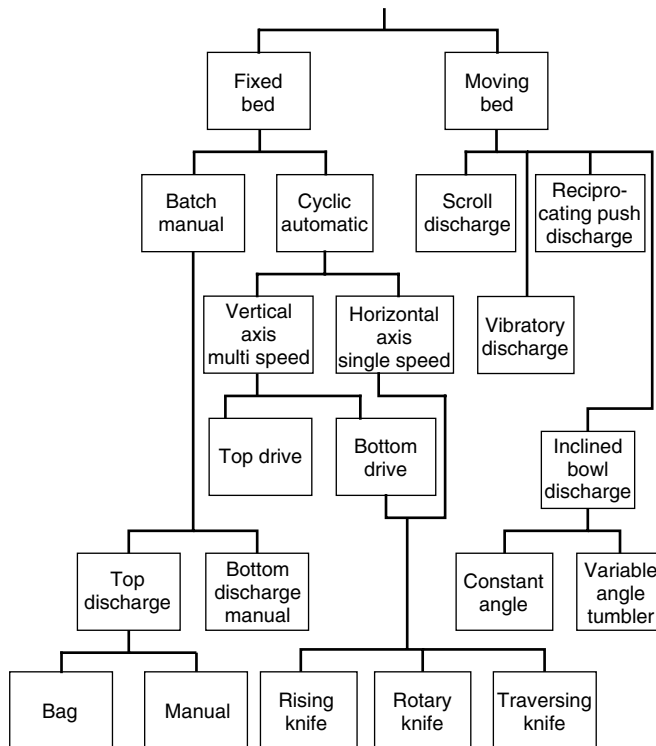


Figure 10.20. Filtration centrifuge family tree (after Bradley, 1965a)

Schematic diagrams of the various types are shown in Figure 10.21. The simplest machines are the basket types (Figures 10.21a, b, c), and these form the basic design from which the other types have been developed (Figures 10.21d to o).

The various arrangements of knife mechanisms used for automatic removal of the cake are shown in Figures 10.21d to h. The bottom discharge-type machines (Figures 10.21d, e) can be designed for variable speed, automatic discharge; and are suitable for use with fragile, or plate or needle-shaped crystals, where it is desirable to avoid breakage or compaction of the bed. They can be loaded and discharged at low speeds, which reduces breakage and compaction of the cake. The single-speed machines (Figures 10.21f, g, h) are used where cakes are thin, and short cycle times are required. They can be designed for high-temperature and pressure operation. When continuous operation is required, the scroll, pusher, or other self-discharge types are used (Figures 10.21i to o). The scroll discharge centrifuge is a low-cost, flexible machine, capable of a wide range of applications; but is not suitable for handling fragile materials.

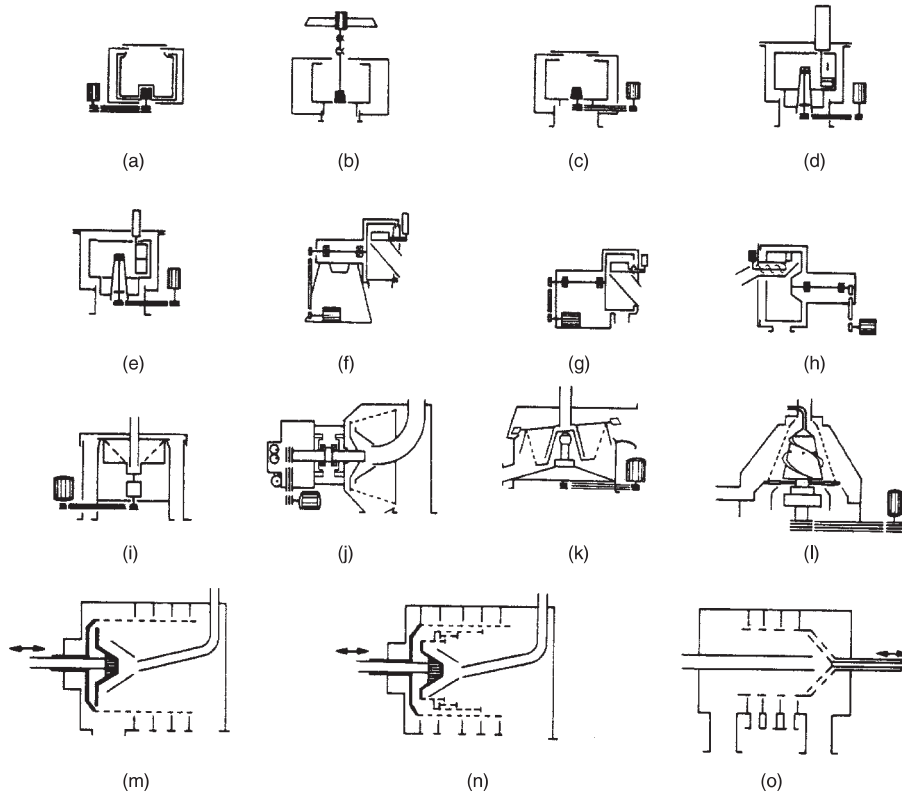


Figure 10.21. Schematic diagrams of filtration centrifuge types (Bradley, 1965) (a) Bottom drive batch basket with bag (b) Top drive bottom discharge batch basket (c) Bottom drive bottom discharge batch basket (d) Bottom drive automatic basket, rising knife (e) Bottom drive automatic basket, rotary knife (f) Single-reversing knife rising knife (g) Single-speed automatic rotary knife (h) Single-speed automatic traversing knife (i) Inclined wall self-discharge (j) Inclined vibrating wall self-discharge (k) Inclined "tumbling" wall self-discharge (l) Inclined wall scroll discharge (m) Traditional single-stage pusher (n) Conical pusher with de-watering cone (o) Conical pusher with de-watering cone

It is normally used for coarse particles, where some contamination of the filtrate with fines can be tolerated.

The capacity of filtration centrifuges is very dependent on the solids concentration in the feed. For example, at 10 per cent feed slurry concentration 9 kg of liquid will be centrifuged for every 1 kg of solids separated; whereas with a 50 per cent solids concentration the quantity will be less than 1 kg. For dilute slurries it is well worth considering using some form of pre-concentration; such as gravity sedimentation or a hydrocyclone.

#### 10.4.4. Hydrocyclones (liquid-cyclones)

Hydrocyclones are used for solid-liquid separations; as well as for solids classification, and liquid-liquid separation. It is a centrifugal device with a stationary wall, the centrifugal force being generated by the liquid motion. The operating principle is basically the same as that

of the gas cyclone described in Section 10.8.3, and in Volume 2, Chapter 8. Hydrocyclones are simple, robust, separating devices, which can be used over the particle size range from 4 to 500  $\mu\text{m}$ . They are often used in groups, as illustrated in Figure 10.24*b*. The design and application of hydrocyclones is discussed fully in books by Abulnaga (2002) and Svarovsky and Thew (1992). Design methods and charts are also given by Zanker (1977), Day *et al.* (1997) and Moir (1985).

The nomographs by Zanker can be used to make a preliminary estimate of the size of cyclone needed. The specialist manufacturers of hydrocyclone equipment should be consulted to determine the best arrangements and design for a particular application.

Zanker's method is outlined below and illustrated in Example 10.2. Figure 10.23 is based on an empirical equation by Bradley (1960):

$$d_{50} = 4.5 \left[ \frac{D_c^3 \mu}{L^{1.2} (\rho_s - \rho_L)} \right] \quad (10.3)$$

where  $d_{50}$  = the particle diameter for which the cyclone is 50 per cent efficient,  $\mu\text{m}$ ,  
 $D_c$  = diameter of the cyclone chamber, cm,

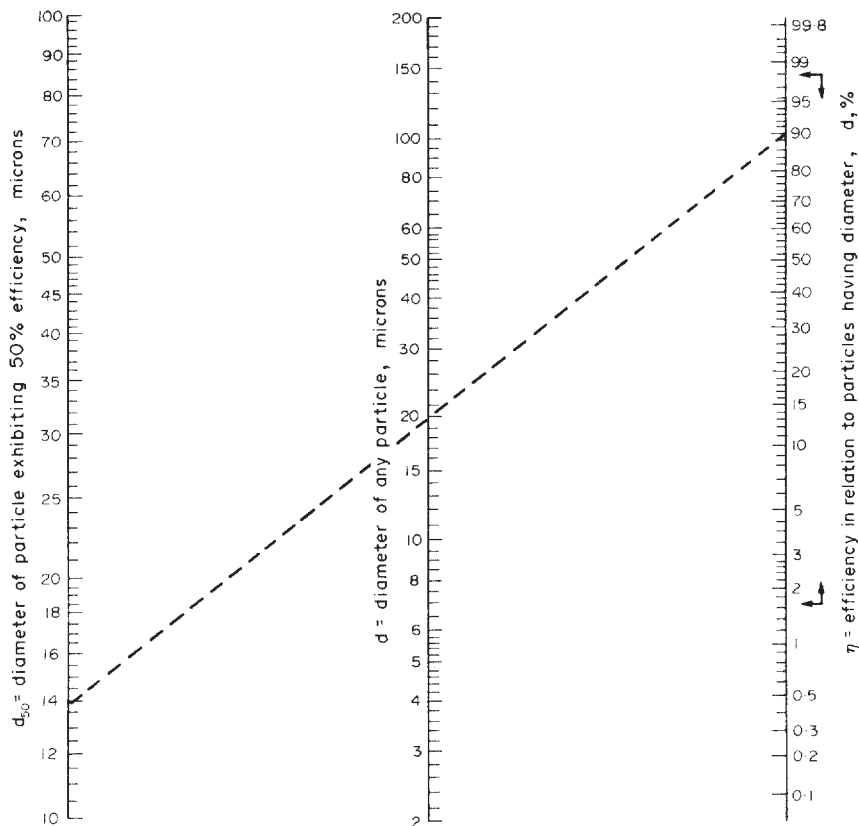


Figure 10.22. Determination of  $d_{50}$  from the desired particle separation (Equation 10.3, Zanker, 1977) (Example 10.2)



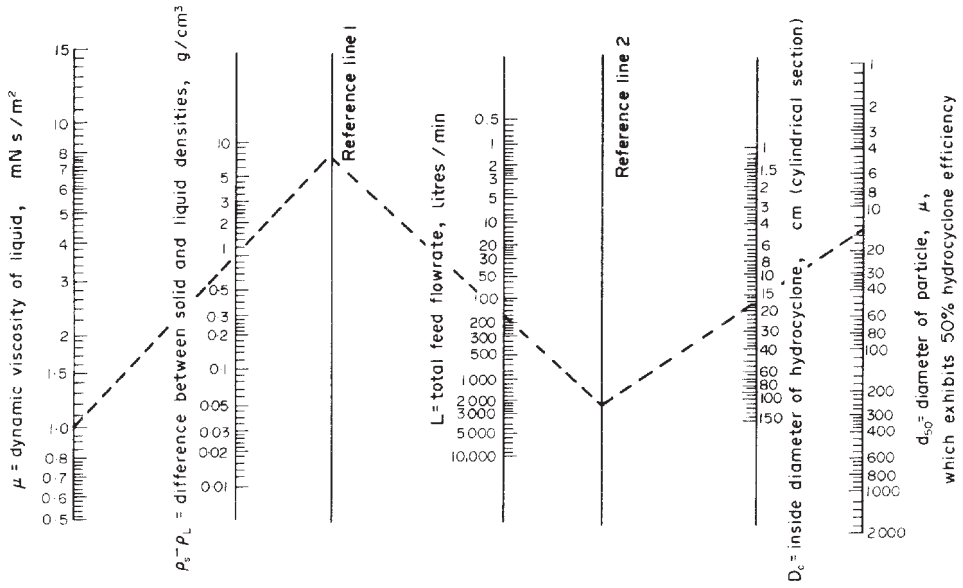


Figure 10.23. Chamber dia.  $D_c$  from flow-rate, physical properties, and  $d_{50}$  particle size (Equation 10.4, Zanker, 1977) (Example 10.2)

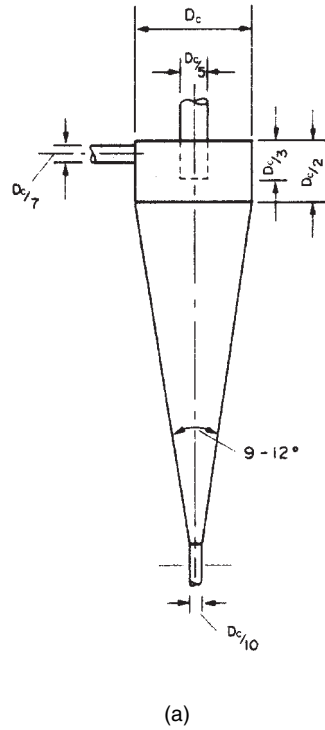


Figure 10.24. (a) Hydrocyclone-typical proportions

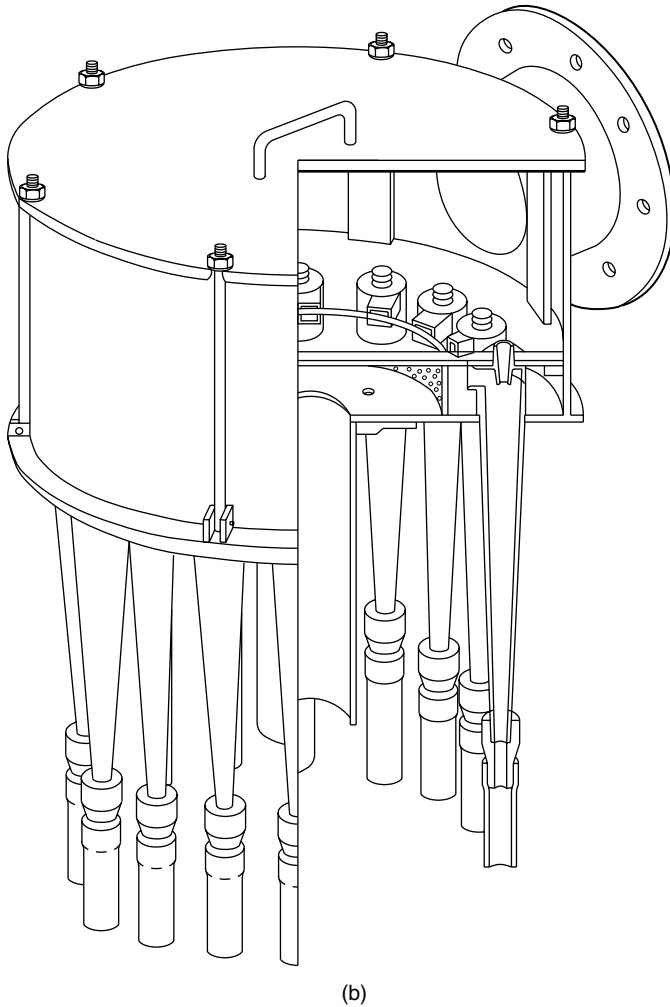


Figure 10.24. (b) A “Clog” assembly of  $16 \times 2$  in (50 mm) diameter hydrocyclone. (Courtesy of Richard Mozley Ltd.)

$\mu$  = liquid viscosity, centipoise ( $\text{mN s/m}^2$ ),

$L$  = feed flow rate, l/min,

$\rho_L$  = density of the liquid,  $\text{g/cm}^3$ ,

$\rho_s$  = density of the solid,  $\text{g/cm}^3$ .

The equation gives the chamber diameter required to separate the so-called  $d_{50}$  particle diameter, as a function of the slurry flow rate and the liquid and solid physical properties. The  $d_{50}$  particle diameter is the diameter of the particle, 50 per cent of which will appear in the overflow, and 50 per cent in the underflow. The separating efficiency for other particles is related to the  $d_{50}$  diameter by Figure 10.22, which is based on a formula by Bennett (1936).

$$\eta = 100 \left[ 1 - e^{-(d/d_{50}-0.115)^3} \right] \quad (10.4)$$

where  $\eta$  = the efficiency of the cyclone in separating any particle of diameter  $d$ ,  
per cent,

$d$  = the selected particle diameter,  $\mu\text{m}$ .

The method applies to hydrocyclones with the proportions shown in Figure 10.24.

### Example 10.2

Estimate the size of hydrocyclone needed to separate 90 per cent of particles with a diameter greater than  $20 \mu\text{m}$ , from  $10 \text{ m}^3/\text{h}$  of a dilute slurry.

Physical properties: solid density  $2000 \text{ kg/m}^3$ , liquid density  $1000 \text{ kg/m}^3$ , viscosity  $1 \text{ mN s/m}^2$

### Solution

$$\text{Flow-rate} = \frac{10 \times 10^3}{60} = 166.71/\text{min}$$

$$(\rho_s - \rho_L) = 2.0 - 1.0 = 1.0 \text{ g/cm}^3$$

From Figure 10.22, for 90 per cent removal of particles above  $20 \mu\text{m}$

$$d_{50} = 14 \mu\text{m}$$

From Figure 10.23, for  $\mu = 1 \text{ mN s/m}^2$ ,  $(\rho_s - \rho_L) = 1.0 \text{ g/cm}^3$ ,  $L = 167/\text{min}$

$$D_c = \underline{\underline{16 \text{ cm}}}$$

### 10.4.5. Pressing (expression)

Pressing, in which the liquid is squeezed (expressed) from a mass of solids by compression, is used for certain specialised applications. Pressing consumes a great deal of energy, and should not be used unless no other separating technique is suitable. However, in some applications dewatering by pressing can be competitive with drying.

Presses are of two basic types: hydraulic batch presses and screw presses. Hydraulic presses are used for extracting fruit juices, and screw presses for dewatering materials; such as paper pulp, rubbish and manure. The equipment used is described in the handbooks; Perry *et al.* (1997).

### 10.4.6. Solids drying

Drying is the removal of water, or other volatile liquids, by evaporation. Most solid materials require drying at some stage in their production. The choice of suitable drying equipment cannot be separated from the selection of the upstream equipment feeding the drying stage.

Table 10.7. Dryer selection

Mode of operation	Generic type	Feed condition			Specific dryer types	Jack-eted	Suitable for heat-sensitive materials	Suitable for vacuum service	Retention or cycle time	Heat transfer method	Capacity	Typical evaporation capacity	
		1	2	3									
Batch	Stationary				1. Shelf		Yes	Yes	6.48 h	Radiant and conduction	Limited	0.15-1.0 kg/hm <sup>2</sup> heat transfer area	
					2. Cabinet	Yes	Yes	Yes	6.48 h	Convection	Limited		
					3. Com-partment				3.12 h	Conduction	Limited		
					Truck	No	Yes	No	4.48 h	Conduction	Limited		
					1. Kettle	Yes	No	Yes	4.48 h	Conduction	Limited		
					2. Pan	Yes	Yes	Yes	3.12 h	Conduction	Limited		
		Drum				Rotary shell	Yes	Yes	Yes	4.48 h	Conduction	Limited	0.5-12
						Rotary internal	Yes	Yes	Yes	4.48 h	Conduction	Limited	
						Double cone	Yes	Yes	Yes	3.12 h	Conduction	Limited	
Continuous	Drum				1. Single drum	No	Yes	Yes	Very short	Conduction	Medium	5-50	
					2. Double drum								
					3. Twin drum								
	Rotary					Rotary direct heat	No	No	No	Long	Convection	High	3-110 kg/hm <sup>3</sup> dryer volume
						Rotary, indirect heat	No	No	No	Long	Conduction	Medium	
						Rotary, steam tube	No	Depends on material	No	Long	Conduction	High	
						Rotary, direct-indirect heat	No	No	No	Long	Conduction	High	
						Louver	No	Depends on material	No	Long	Convection	High	
	Conveyor					Tunnel belt, screen	No	Yes	No	Long	Convection	Medium	1.5-35 kg/hm <sup>2</sup>
						Rotary shelf	Yes	Depends on material	No	Medium	Conduction	Medium	
					Trough	Yes	Depends on material	Yes	Varies	Conduction	Medium		
					Vibrating	Yes	Depends on material	No	Medium	Convection	Medium		
Suspended particle					Turbo	No	Depends on material	No	Medium	Convection	Medium	0.5-100 kg/hm <sup>3</sup>	
					Spray	No	Yes	No	Short	Convection	High		
					Flash bed	No	Yes	No	Short	Convection	High		
					Fluid bed	No	Yes	No	Short	Convection	Medium	1.5-50 kg/hm <sup>3</sup>	

← → = applicable to feed conditions noted

Key to feed conditions:

1. Solutions, colloidal suspensions and emulsions, pumpable solids suspensions, pastes and sludges.
2. Free-flowing powders, granular, crystalline or fibrous solids that can withstand mechanical handling.
3. Solids incapable of withstanding mechanical handling.

The overriding consideration in the selection of drying equipment is the nature and concentration of the feed. Drying is an energy-intensive process, and the removal of liquid by thermal drying will be more costly than by mechanical separation techniques.

Drying equipment can be classified according to the following design and operating features:

1. Batch or continuous.
2. Physical state of the feed: liquid, slurry, wet solid.
3. Method of conveyance of the solid: belt, rotary, fluidised.
4. Heating system: conduction, convection, radiation.

Except for a few specialised applications, hot air is used as the heating and mass transfer medium in industrial dryers. The air may be directly heated by the products of combustion of the fuel used (oil, gas or coal) or indirectly heated, usually by banks of steam-heated finned tubes. The heated air is usually propelled through the dryer by electrically driven fans.

Table 10.7, adapted from a similar selection guide by Parker (1963a), shows the basic features of the various types of solids dryer used in the process industries; and Table 10.8, by Williams-Gardner (1965), shows typical applications.

Batch dryers are normally used for small-scale production and where the drying cycle is likely to be long. Continuous dryers require less labour, less floor space; and produce a more uniform quality product.

When the feed is solids, it is important to present the material to the dryer in a form that will produce a bed of solids with an open, porous, structure.

For pastes and slurries, some form of pretreatment equipment will normally be needed, such as extrusion or granulation.

The main factors to be considered when selecting a dryer are:

1. Feed condition: solid, liquid, paste, powder, crystals.
2. Feed concentration, the initial liquid content.
3. Product specification: dryness required, physical form.
4. Throughput required.
5. Heat sensitivity of the product.
6. Nature of the vapour: toxicity, flammability.
7. Nature of the solid: flammability (dust explosion hazard), toxicity.

The drying characteristics of the material can be investigated by laboratory and pilot plant tests; which are best carried out in consultation with the equipment vendors.

The theory of drying processes is discussed in Volume 2, Chapter 16. Full descriptions of the various types of dryer and their applications are given in that chapter and in Perry *et al.* (1997) and Walas (1990). Only brief descriptions of the principal types will be given in this section.

The basic types used in the chemical process industries are: tray, band, rotary, fluidised, pneumatic, drum and spray dryers.

### **Tray dryers (Figure 10.25)**

Batch tray dryers are used for drying small quantities of solids, and are used for a wide range of materials.

Table 10.8. Dryer applications

<i>Dryer type</i>	<i>System</i>	<i>Feed form</i>	<i>Typical products</i>
Batch ovens	Forced convection	Paste, granules, extrude cake	Pigment dyestuffs, pharmaceuticals, fibres
	Vacuum	Extrude cake	Pharmaceuticals
„ pan (agitated)	Atmospheric and vacuum	Crystals, granules, powders	Fine chemicals, food products
„ rotary	Vacuum	Crystals, granules solvent recovery	Pharmaceuticals
„ fluid bed	Forced convection	Granular, crystals	Fine chemicals, pharmaceuticals, plastics
„ infra-red	Radiant	Components sheets	Metal products, plastics
Continuous rotary	Convection Direct/indirect Direct Indirect Conduction	Crystals, coarse powders, extrudes, preformed cake lumps, granular paste and fillers, cakes back-mixed with dry product	Chemical ores, food products, clays, pigments, chemicals  Carbon black
„ film drum	Conduction	Liquids, suspensions	Foodstuffs, pigment
„ trough	Conduction		Ceramics, adhesives
„ spray	Convection	Liquids, suspensions	Foodstuffs, pharmaceuticals, ceramics, fine chemicals, detergents, organic extracts
„ band	Convection	Preformed solids	Foodstuffs, pigments, chemicals, rubber, clays, ores, textiles
„ fluid bed	Convection	Preformed solids granules, crystals	Ores, coal, clays, chemicals
„ pneumatic	Convection	Preformed pastes, granules, crystals, coarse products	Chemicals, starch, flour, resins, wood-products, food products
„ infra-red	Radiant	Components sheets	Metal products, moulded fibre articles, painted surfaces

The material to be dried is placed in solid bottomed trays over which hot air is blown; or perforated bottom trays through which the air passes.

Batch dryers have high labour requirements, but close control can be maintained over the drying conditions and the product inventory, and they are suitable for drying valuable products.

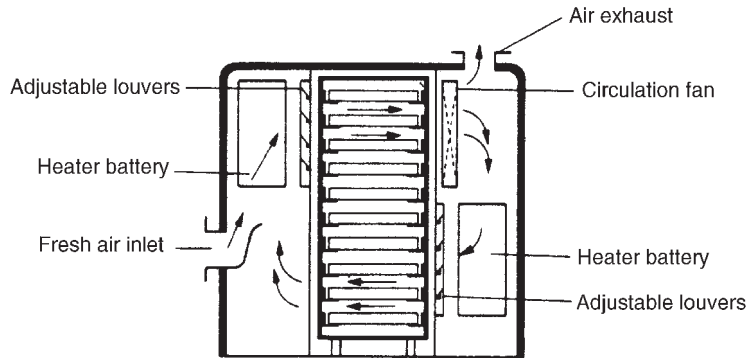


Figure 10.25. Tray dryer

### **Conveyor dryers (continuous circulation band dryers) (Figure 10.26)**

In this type, the solids are fed on to an endless, perforated, conveyor belt, through which hot air is forced. The belt is housed in a long rectangular cabinet, which is divided up into zones, so that the flow pattern and temperature of the drying air can be controlled. The relative movement through the dryer of the solids and drying air can be parallel or, more usually, counter-current.

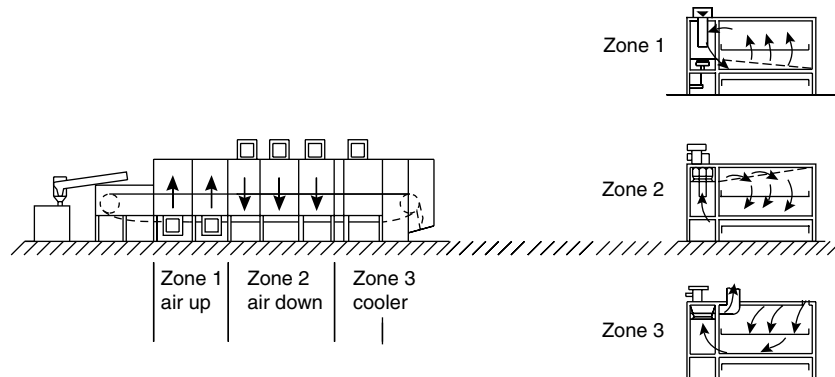


Figure 10.26. Conveyor dryer

This type of dryer is clearly only suitable for materials that form a bed with an open structure. High drying rates can be achieved, with good product-quality control. Thermal efficiencies are high and, with steam heating, steam usage can be as low as 1.5 kg per kg of water evaporated. The disadvantages of this type of dryer are high initial cost and, due to the mechanical belt, high maintenance costs.

### **Rotary dryer (Figure 10.27)**

In rotary dryers the solids are conveyed along the inside of a rotating, inclined, cylinder and are heated and dried by direct contact with hot air gases flowing through the cylinder. In some, the cylinders are indirectly heated.

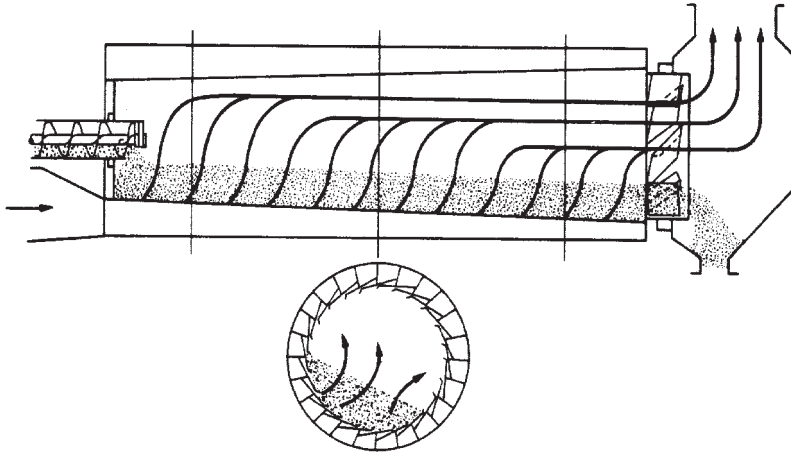


Figure 10.27. Rotary dryer

Rotating dryers are suitable for drying free-flowing granular materials. They are suitable for continuous operation at high throughputs; have a high thermal efficiency and relatively low capital cost and labour costs. Some disadvantages of this type are: a non-uniform residence time, dust generation and high noise levels.

### Fluidised bed dryers (Figure 10.28)

In this type of dryer, the drying gas is passed through the bed of solids at a velocity sufficient to keep the bed in a fluidised state; which promotes high heat transfer and drying rates.

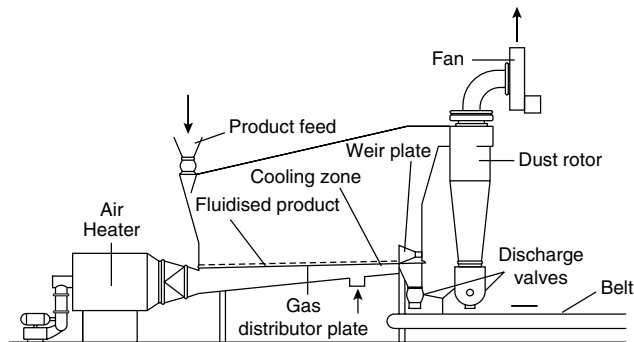


Figure 10.28. Fluidised bed dryer

Fluidised bed dryers are suitable for granular and crystalline materials within the particle size range 1 to 3 mm. They are designed for continuous and batch operation.

The main advantages of fluidised dryers are: rapid and uniform heat transfer; short drying times, with good control of the drying conditions; and low floor area requirements. The power requirements are high compared with other types.



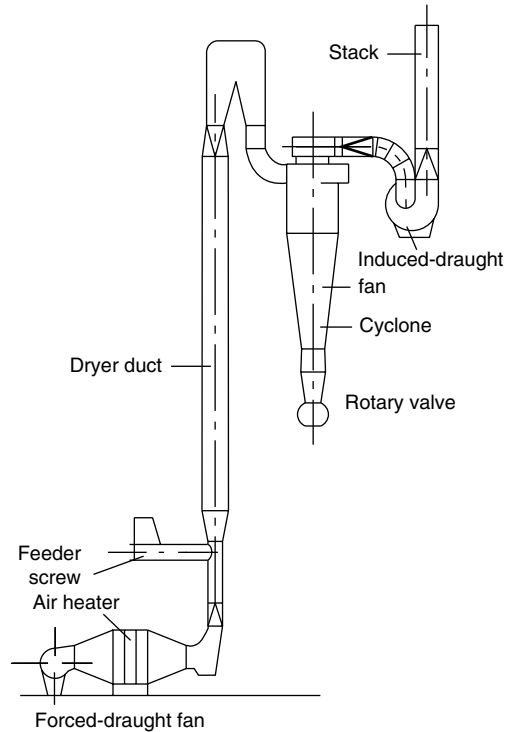


Figure 10.29. Pneumatic dryer

### ***Pneumatic dryers (Figure 10.29)***

Pneumatic dryers, also called flash dryers, are similar in their operating principle to spray dryers. The product to be dried is dispersed into an upward-flowing stream of hot gas by a suitable feeder. The equipment acts as a pneumatic conveyor and dryer. Contact times are short, and this limits the size of particle that can be dried. Pneumatic dryers are suitable for materials that are too fine to be dried in a fluidised bed dryer but which are heat sensitive and must be dried rapidly. The thermal efficiency of this type is generally low.

### ***Spray dryers (Figure 10.30)***

Spray dryers are normally used for liquid and dilute slurry feeds, but can be designed to handle any material that can be pumped. The material to be dried is atomised in a nozzle, or by a disc-type atomiser, positioned at the top of a vertical cylindrical vessel. Hot air flows up the vessel (in some designs downward) and conveys and dries the droplets. The liquid vaporises rapidly from the droplet surface and open, porous particles are formed. The dried particles are removed in a cyclone separator or bag filter.

The main advantages of spray drying are the short contact time, making it suitable for drying heat-sensitive materials, and good control of the product particle size, bulk density, and form. Because the solids concentration in the feed is low the heating requirements will be high. Spray drying is discussed in a book by Masters (1991).

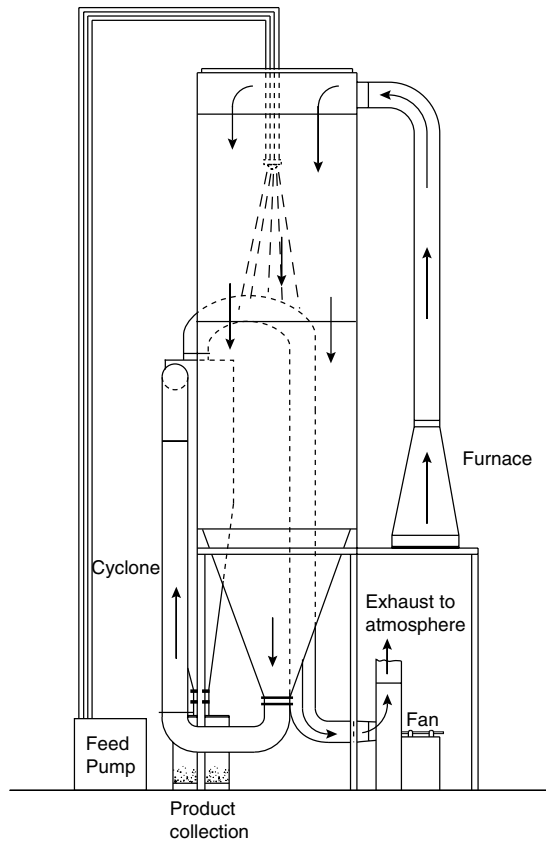


Figure 10.30. Spray dryer

### ***Rotary drum dryers (Figure 10.31)***

Drum dryers are used for liquid and dilute slurry feeds. They are an alternative choice to spray dryers when the material to be dried will form a film on a heated surface, and is not heat sensitive.

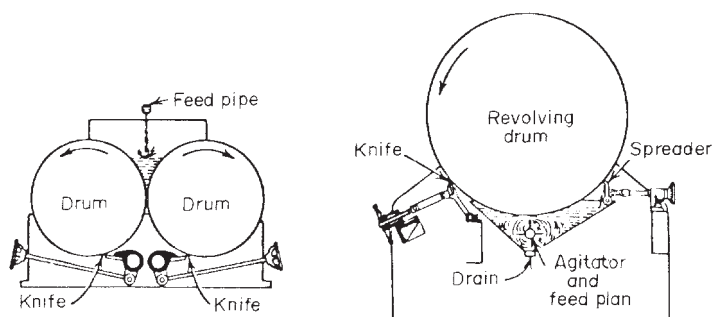


Figure 10.31. Rotary drum dryers

They consist essentially of a revolving, internally heated, drum, on which a film of the solids is deposited and dried. The film is formed either by immersing part of the drum in a trough of the liquid or by spraying, or splashing, the feed on to the drum surface; double drums are also used in which the feed is fed into the “nip” formed between the drums.

The drums are usually heated with steam, and steam economies of 1.3 kg steam per kg of water evaporated are typically achieved.

## 10.5. SEPARATION OF DISSOLVED SOLIDS

On an industrial scale, evaporation and crystallisation are the main processes used for the recovery of dissolved solids from solutions.

Membrane filtration processes, such as reverse osmosis, and micro and ultra filtration, are used to “filter out” dissolved solids in certain applications; see Table 10.9. These specialised processes will not be discussed in this book. A comprehensive description of the techniques used and their applications is given in Volume 2, Chapter 8; see also: Scott and Hughes (1995), Cheryan (1986), McGregor (1986) and Porter (1997).

Table 10.9. Membrane filtration process

Process	Approximate size range (m)	Applications
Microfiltration	$10^{-8}$ to $10^{-4}$	pollen, bacteria, blood cells
Ultrafiltration	$10^{-9}$ to $10^{-8}$	proteins and virus
Nanofiltration	$5 \times 10^{-9}$ to $15 \times 10^{-9}$	water softening
Reverse osmosis	$10^{-10}$ to $10^{-9}$	desalination
Dialysis	$10^{-9}$ to molecules	blood purification
Electrodialysis	$10^{-9}$ to molecules	separation of electrolytes
Pervaporation	$10^{-9}$ to molecules	dehydration of ethanol
Gas permeation	$10^{-9}$ to molecules	hydrogen recovery, dehydration

### 10.5.1. Evaporators

Evaporation is the removal of a solvent by vaporisation, from solids that are not volatile. It is normally used to produce a concentrated liquid, often prior to crystallisation, but a dry solid product can be obtained with some specialised designs. The general subject of evaporation is covered in Volume 2, Chapter 14. That chapter includes a discussion of heat transfer in evaporators, multiple-effect evaporators, and a description of the principal types of equipment. The selection of the appropriate type of evaporator is discussed by Cole (1984). Evaporation is the subject of a book by Billet (1989).

A great variety of evaporator designs have been developed for specialised applications in particular industries. The designs can be grouped into the following basic types.

#### ***Direct-heated evaporators***

This type includes solar pans and submerged combustion units. Submerged combustion evaporators can be used for applications where contamination of the solution by the products of combustion is acceptable.

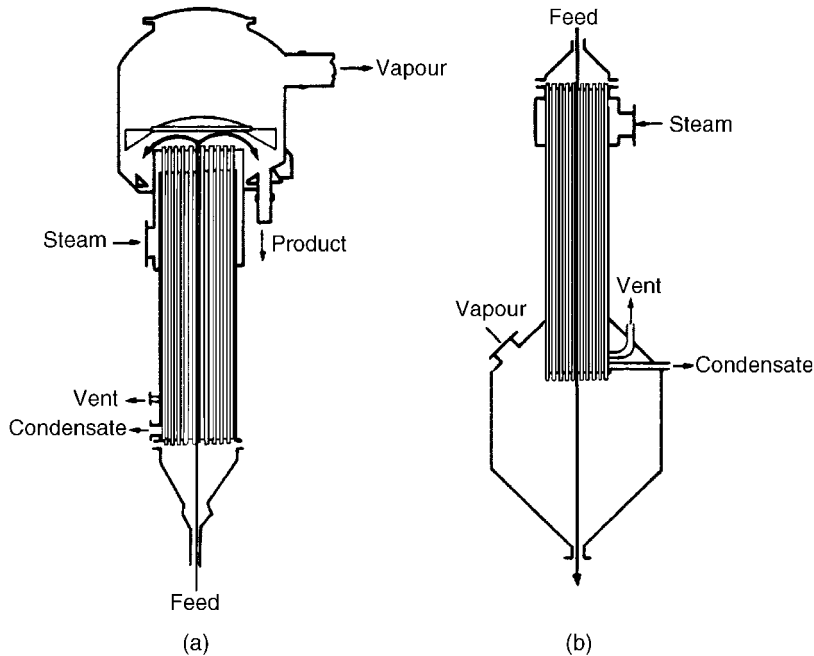


Figure 10.32. Long-tube evaporators (a) Rising film (b) Falling film

### ***Long-tube evaporators (Figure 10.32)***

In this type the liquid flows as a thin film on the walls of a long, vertical, heated, tube. Both falling film and rising film types are used. They are high capacity units; suitable for low viscosity solutions.

### ***Forced-circulation evaporators (Figure 10.33)***

In forced circulation evaporators the liquid is pumped through the tubes. They are suitable for use with materials which tend to foul the heat transfer surfaces, and where crystallisation can occur in the evaporator.

### ***Agitated thin-film evaporators (Figure 10.34)***

In this design a thin layer of solution is spread on the heating surface by mechanical means. Wiped-film evaporators are used for very viscous materials and for producing solid products. The design and applications of this type of evaporator are discussed by Mutzenburg (1965), Parker (1965) and Fischer (1965).

### ***Short-tube evaporators***

Short-tube evaporators, also called callandria evaporators, are used in the sugar industry; see Volume 2.

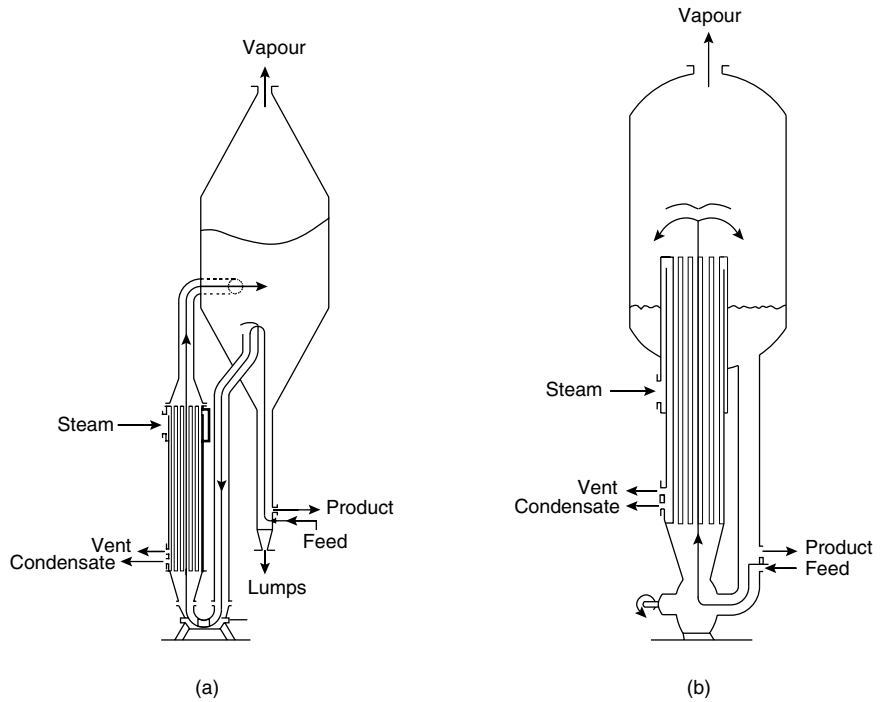


Figure 10.33. Forced-circulation evaporators (a) Submerged tube (b) Boiling tube

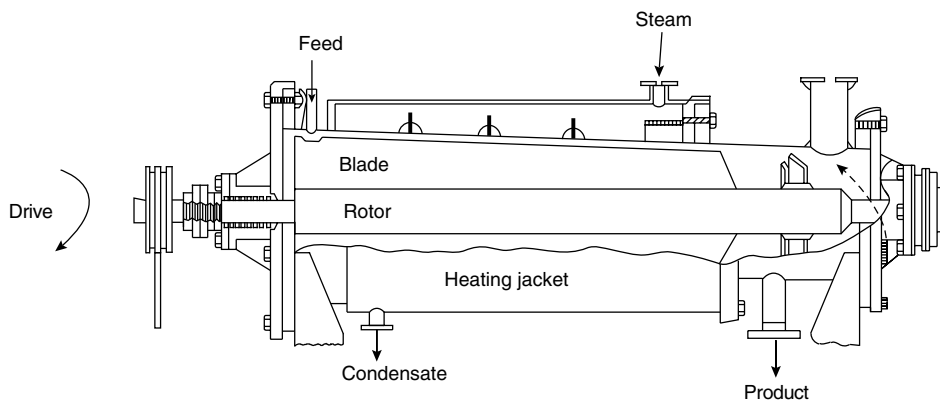


Figure 10.34. Horizontal wiped-film evaporator

### **Evaporator selection**

The selection of the most suitable evaporator type for a particular application will depend on the following factors:

1. The throughput required.
2. The viscosity of the feed and the increase in viscosity during evaporation.

3. The nature of the product required; solid, slurry, or concentrated solution.
4. The heat sensitivity of the product.
5. Whether the materials are fouling or non-fouling.
6. Whether the solution is likely to foam.
7. Whether direct heating can be used.

A selection guide based on these factors is given in Figure 10.35; see also Parker (1963*b*).

Evaporator type	Feed conditions							Suitable for heat-sensitive materials
	Viscosity, mN s/m <sup>2</sup>			Foaming	Scaling or fouling	Crystals produced	Solids in suspension	
Very viscous > 1000	Medium viscosity < 1000 max	Low viscosity < 100						
Recirculating Calandria (short vertical tube)								No
Forced circulation								Yes
Falling film								No
Natural circulation								No
Single pass wiped film								Yes
Tubular (long tube) Falling film								Yes
Rising film								Yes

Figure 10.35. Evaporator selection guide

### Auxilliary equipment

Condensers and vacuum pumps will be needed for evaporators operated under vacuum. For aqueous solutions, steam ejectors and jet condensers are normally used. Jet condensers are direct-contact condensers, where the vapour is condensed by contact with jets of cooling water. Indirect, surface condensers, are used where it is necessary to keep the condensed vapour and cooling water effluent separate.

### 10.5.2. Crystallisation

Crystallisation is used for the production, purification and recovery of solids. Crystalline products have an attractive appearance, are free flowing, and easily handled and packaged. The process is used in a wide range of industries: from the small-scale production of specialised chemicals, such as pharmaceutical products, to the tonnage production of products such as sugar, common salt and fertilisers.

Crystallisation theory is covered in Volume 2, Chapter 15 and in other texts: Mullin (2001) and Jones (2002). Descriptions of the various crystallisers used commercially can be found in these texts and in handbooks: Mersmann (2001), Perry *et al.* (1997) and

Schweitzer (1997). Procedures for the scale-up and design of crystallisers are given by Mersmann (2001), and Mersham (1988), (1984).

Precipitation, which can be considered as a branch of crystallisation, is covered by Sohnel and Garside (1992).

Crystallisation equipment can be classified by the method used to obtain supersaturation of the liquor, and also by the method used to suspend the growing crystals. Supersaturation is obtained by cooling or evaporation. There are four basic types of crystalliser; these are described briefly below.

### **Tank crystallisers**

This is the simplest type of industrial crystallising equipment. Crystallisation is induced by cooling the mother liquor in tanks; which may be agitated and equipped with cooling coils or jackets. Tank crystallisers are operated batchwise, and are generally used for small-scale production.

### **Scraped-surface crystallisers**

This type is similar in principle to the tank type, but the cooling surfaces are continually scraped or agitated to prevent the fouling by deposited crystals and to promote heat transfer. They are suitable for processing high-viscosity liquors. Scraped-surface

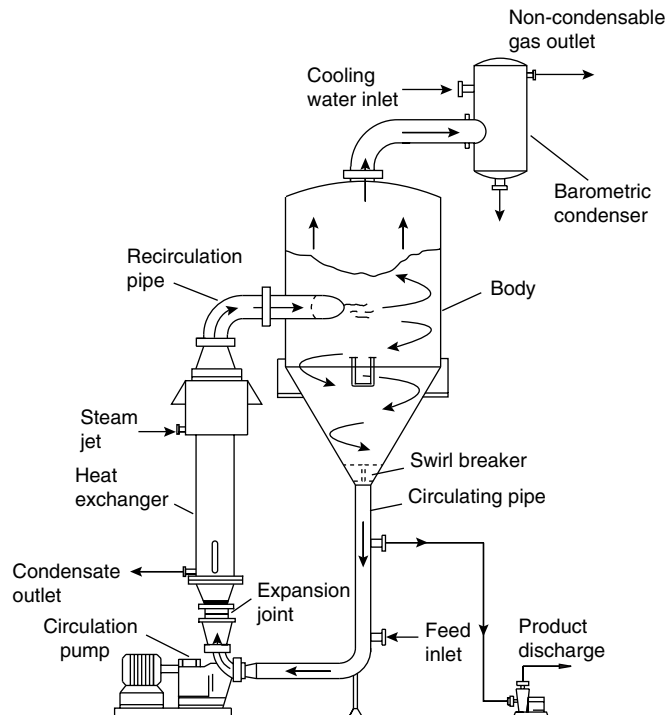


Figure 10.36. Circulating magma crystalliser (evaporative type)

crystallisers can be operated batchwise, with recirculation of the mother liquor, or continuously. A disadvantage of this type is that they tend to produce very small crystals.

### ***Circulating magma crystallisers (Figure 10.36)***

In this type both the liquor and growing crystals are circulated through the zone in which supersaturation occurs. Circulating magma crystallisers are probably the most important type of large-scale crystallisers used in the chemical process industry. Designs are available in which supersaturation is achieved by direct cooling, evaporation or evaporative cooling under vacuum.

### ***Circulating liquor crystallisers (Figure 10.37)***

In this type only the liquor is circulated through the heating or cooling equipment; the crystals are retained in suspension in the crystallising zone by the up-flow of liquor. Circulating liquor crystallisers produce crystals of regular size. The basic design consists of three components: a vessel in which the crystals are suspended and grow and are removed; a means of producing supersaturation, by cooling or evaporation; and a means of circulating the liquor. The Oslo crystalliser (Figure 10.37) is the archetypal design for this type of crystallising equipment.

Circulating liquor crystallisers and circulating magma crystallisers are used for the large-scale production of a wide range of crystal products.

Typical applications of the main types of crystalliser are summarised in Table 10.10 (see page 440); see also Larson (1978).

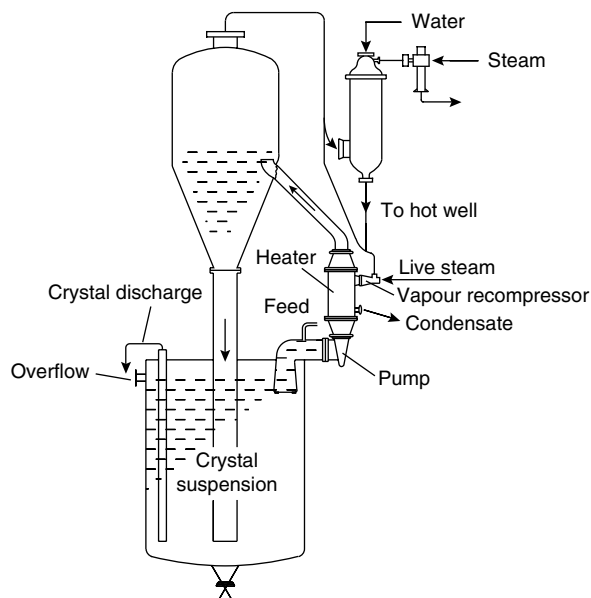


Figure 10.37. Oslo evaporative crystalliser



Table 10.10. Selection of crystallisers

Crystalliser type	Applications	Typical uses
Tank	Batch operation, small-scale production	Fatty acids, vegetable oils, sugars
Scraped surface	Organic compounds, where fouling is a problem, viscous materials	Chlorobenzenes, organic acids, paraffin waxes, naphthalene, urea
Circulating magma	Production of large-sized crystals. High throughputs	Ammonium and other inorganic salts, sodium and potassium chlorides
Circulating liquor	Production of uniform crystals (smaller size than circulating magma). High throughputs.	Gypsum, inorganic salts, sodium and potassium nitrates, silver nitrates

## 10.6. LIQUID-LIQUID SEPARATION

Separation of two liquid phases, immiscible or partially miscible liquids, is a common requirement in the process industries. For example, in the unit operation of liquid-liquid extraction the liquid contacting step must be followed by a separation stage (Chapter 11, Section 11.16). It is also frequently necessary to separate small quantities of entrained water from process streams. The simplest form of equipment used to separate liquid phases is the gravity settling tank, the decanter. Various proprietary equipment is also used to promote coalescence and improve separation in difficult systems, or where emulsions are likely to form. Centrifugal separators are also used.

### 10.6.1. Decanters (settlers)

Decanters are used to separate liquids where there is a sufficient difference in density between the liquids for the droplets to settle readily. Decanters are essentially tanks which give sufficient residence time for the droplets of the dispersed phase to rise (or settle) to the interface between the phases and coalesce. In an operating decanter there will be three distinct zones or bands: clear heavy liquid; separating dispersed liquid (the dispersion zone); and clear light liquid.

Decanters are normally designed for continuous operation, but the same design principles will apply to batch operated units. A great variety of vessel shapes is used for decanters, but for most applications a cylindrical vessel will be suitable, and will be the cheapest shape. Typical designs are shown in Figures 10.38 and 10.39. The position of the interface can be controlled, with or without the use of instruments, by use of a syphon take-off for the heavy liquid, Figure 10.38.

The height of the take-off can be determined by making a pressure balance. Neglecting friction loss in the pipes, the pressure exerted by the combined height of the heavy and light liquid in the vessel must be balanced by the height of the heavy liquid in the take-off leg, Figure 10.38.

$$(z_1 - z_3)\rho_1 g + z_3\rho_2 g = z_2\rho_2 g$$

hence

$$z_2 = \frac{(z_1 - z_3)\rho_1}{\rho_2} + z_3 \quad (10.5)$$

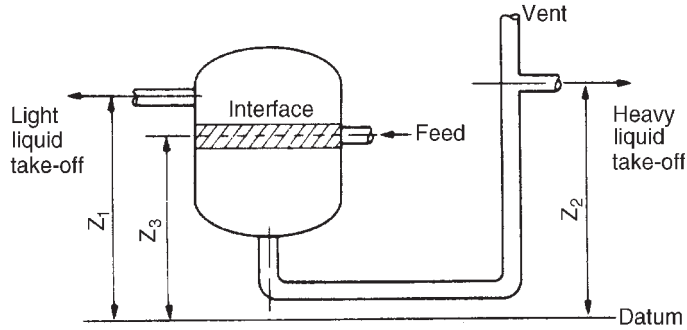


Figure 10.38. Vertical decanter

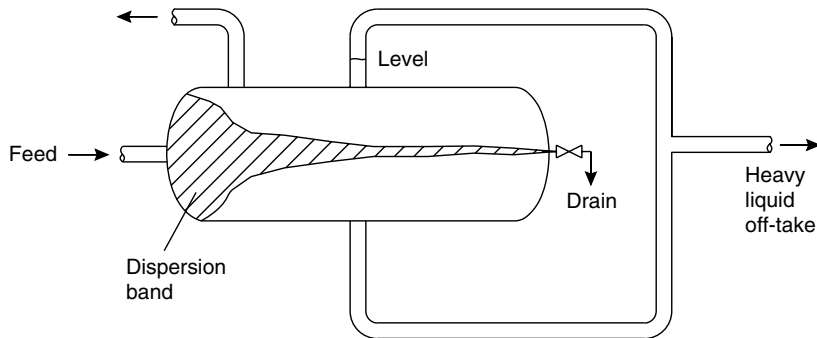


Figure 10.39. Horizontal decanter

- where  $\rho_1$  = density of the light liquid,  $\text{kg/m}^3$ ,  
 $\rho_2$  = density of the heavy liquid,  $\text{kg/m}^3$ ,  
 $z_1$  = height from datum to light liquid overflow, m,  
 $z_2$  = height from datum to heavy liquid overflow, m,  
 $z_3$  = height from datum to the interface, m.

The height of the liquid interface should be measured accurately when the liquid densities are close, when one component is present only in small quantities, or when the throughput is very small. A typical scheme for the automatic control of the interface, using a level instrument that can detect the position of the interface, is shown in Figure 10.40. Where one phase is present only in small amounts it is often recycled to the decanter feed to give more stable operation.

### **Decanter design**

A rough estimate of the decanter volume required can be made by taking a hold-up time of 5 to 10 min, which is usually sufficient where emulsions are not likely to form. Methods

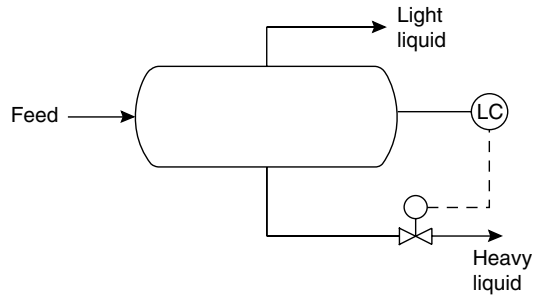


Figure 10.40. Automatic control, level controller detecting interface

for the design of decanters are given by Hooper (1997) and Signales (1975). The general approach taken is outlined below and illustrated by Example 10.3.

The decanter vessel is sized on the basis that the velocity of the continuous phase must be less than settling velocity of the droplets of the dispersed phase. Plug flow is assumed, and the velocity of the continuous phase calculated using the area of the interface:

$$u_c = \frac{L_c}{A_i} < u_d \quad (10.6)$$

where  $u_d$  = settling velocity of the dispersed phase droplets, m/s,

$u_c$  = velocity of the continuous phase, m/s,

$L_c$  = continuous phase volumetric flow rate, m<sup>3</sup>/s,

$A_i$  = area of the interface, m<sup>2</sup>.

Stokes' law (see Volume 2, Chapter 3) is used to determine the settling velocity of the droplets:

$$u_d = \frac{d_d^2 g (\rho_d - \rho_c)}{18 \mu_c} \quad (10.7)$$

where  $d_d$  = droplet diameter, m,

$u_d$  = settling (terminal) velocity of the dispersed phase droplets with diameter  $d$ , m/s,

$\rho_c$  = density of the continuous phase, kg/m<sup>3</sup>,

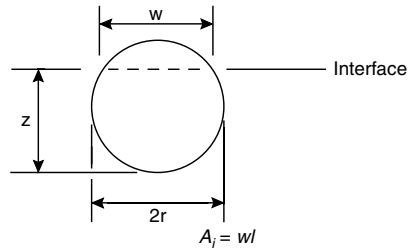
$\rho_d$  = density of the dispersed phase, kg/m<sup>3</sup>,

$\mu_c$  = viscosity of the continuous phase, N s/m<sup>2</sup>,

$g$  = gravitational acceleration, 9.81 m/s<sup>2</sup>.

Equation 10.7 is used to calculate the settling velocity with an assumed droplet size of 150  $\mu$ m, which is well below the droplet sizes normally found in decanter feeds. If the calculated settling velocity is greater than  $4 \times 10^{-3}$  m/s, then a figure of  $4 \times 10^{-3}$  m/s is used.

For a horizontal, cylindrical, decanter vessel, the interfacial area will depend on the position of the interface.



and

$$w = 2(2rz - z^2)^{1/2}$$

where  $w$  = width of the interface, m,

$z$  = height of the interface from the base of the vessel, m,

$l$  = length of the cylinder, m,

$r$  = radius of the cylinder, m.

For a vertical, cylindrical decanter:

$$A_i = \pi r^2$$

The position of the interface should be such that the band of droplets that collect at the interface waiting to coalesce and cross the interface does not extend to the bottom (or top) of the vessel. Ryon *et al.* (1959) and Mizrahi and Barnea (1973) have shown that the depth of the dispersion band is a function of the liquid flow rate and the interfacial area. A value of 10 per cent of the decanter height is usually taken for design purposes. If the performance of the decanter is likely to be critical the design can be investigated using scale models. The model should be scaled to operate at the same Reynolds number as the proposed design, so that the effect of turbulence can be investigated; see Hooper (1975).

### Example 10.3

Design a decanter to separate a light oil from water.

The oil is the dispersed phase.

Oil, flow rate 1000 kg/h, density 900 kg/m<sup>3</sup>, viscosity 3 mN s/m<sup>2</sup>.

Water, flow rate 5000 kg/h, density 1000 kg/m<sup>3</sup>, viscosity 1 mN s/m<sup>2</sup>.

### Solution

Take  $d_d = 150 \mu\text{m}$

$$u_d = \frac{(150 \times 10^{-6})^2 9.81 (900 - 1000)}{18 \times 1 \times 10^{-3}} \quad (10.7)$$

$$= -0.0012 \text{ m/s, } -1.2 \text{ mm/s (rising)}$$

As the flow rate is small, use a vertical, cylindrical vessel.

$$L_c = \frac{5000}{1000} \times \frac{1}{3600} = 1.39 \times 10^{-3} \text{ m}^3/\text{s}$$

$$u_c \neq u_d, \text{ and } u_c = \frac{L_c}{A_i}$$

hence 
$$A_i = \frac{1.39 \times 10^{-3}}{0.0012} = 1.16 \text{ m}^2$$

$$r = \sqrt{\frac{1.16}{\pi}} = 0.61 \text{ m}$$

$$\text{diameter} = \underline{\underline{1.2 \text{ m}}}$$

Take the height as twice the diameter, a reasonable value for a cylinder:

$$\text{height} = \underline{\underline{2.4 \text{ m}}}$$

Take the dispersion band as 10 per cent of the height = 0.24 m

Check the residence time of the droplets in the dispersion band

$$= \frac{0.24}{u_d} = \frac{0.24}{0.0012} = 200 \text{ s } (\sim 3 \text{ min})$$

This is satisfactory, a time of 2 to 5 min is normally recommended. Check the size of the water (continuous, heavy phase) droplets that could be entrained with the oil (light phase).

$$\begin{aligned} \text{Velocity of oil phase} &= \frac{1000}{900} \times \frac{1}{3600} \times \frac{1}{1.16} \\ &= 2.7 \times 10^{-4} \text{ m/s } (0.27 \text{ mm/s}) \end{aligned}$$

From equation 10.7

$$d_d = \left[ \frac{u_d 18 \mu_c}{g(\rho_d - \rho_c)} \right]^{1/2}$$

so the entrained droplet size will

$$\begin{aligned} &= \left[ \frac{2.7 \times 10^{-4} \times 18 \times 3 \times 10^{-3}}{9.81(1000 - 900)} \right]^{1/2} \\ &= \underline{\underline{1.2 \times 10^{-4} \text{ m}}} = 120 \text{ } \mu\text{m} \end{aligned}$$

which is satisfactory; below 150  $\mu\text{m}$ .

### ***Piping arrangement***

To minimise entrainment by the jet of liquid entering the vessel, the inlet velocity for a decanter should keep below 1 m/s.

$$\text{Flow-rate} = \left[ \frac{1000}{900} + \frac{5000}{1000} \right] \frac{1}{3600} = 1.7 \times 10^{-3} \text{ m}^3/\text{s}$$

$$\text{Area of pipe} = \frac{1.7 \times 10^{-3}}{1} = 1.7 \times 10^{-3} \text{ m}^2$$

$$\text{Pipe diameter} = \sqrt{\frac{1.7 \times 10^{-3} \times 4}{\pi}} = 0.047 \text{ m, say } \underline{\underline{50 \text{ mm}}}$$

Take the position of the interface as half-way up the vessel and the light liquid off-take as at 90 per cent of the vessel height, then

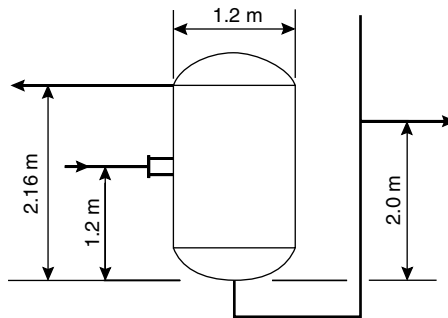
$$z_1 = 0.9 \times 2.4 = 2.16 \text{ m}$$

$$z_3 = 0.5 \times 2.4 = 1.2 \text{ m}$$

$$z_2 = \frac{(2.16 - 1.2)}{1000} \times 900 + 1.2 = \underline{\underline{2.06 \text{ m}}} \quad (10.5)$$

say 2.0 m

Proposed design



Drain valves should be fitted at the interface so that any tendency for an emulsion to form can be checked; and the emulsion accumulating at the interface drained off periodically as necessary.

### 10.6.2. Plate separators

Stacks of horizontal, parallel, plates are used in some proprietary decanter designs to increase the interfacial area per unit volume and to reduce turbulence. They, in effect, convert the decanter volume into several smaller separators connected in parallel.

### 10.6.3. Coalescers

Proprietary equipment, in which the dispersion is forced through some form of coalescing medium, is often used for the coalescence and separation of finely dispersed droplets. A medium is chosen that is preferentially wetted by the dispersed phase; knitted wire or plastic mesh, beds of fibrous material, or special membranes are used. The coalescing medium works by holding up the dispersed droplets long enough for them to form globlets of sufficient size to settle. A typical unit is shown in Figure 10.41; see Redmon (1963). Coalescing filters are suitable for separating small quantities of dispersed liquids from large throughputs.

Electrical coalescers, in which a high voltage field is used to break down the stabilising film surrounding the suspended droplets, are used for desalting crude oils and for similar applications; see Waterman (1965).

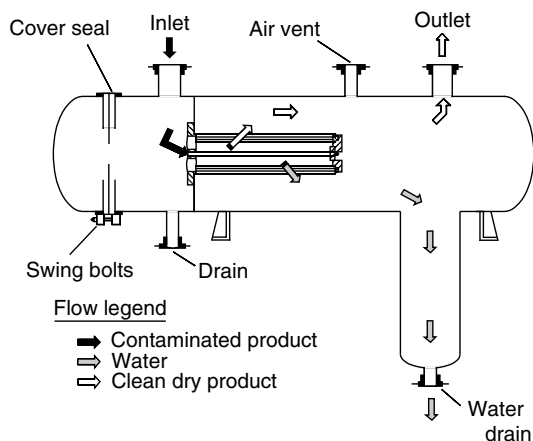


Figure 10.41. Typical coalescer design

## 10.6.4. Centrifugal separators

### *Sedimentation centrifuges*

For difficult separations, where simple gravity settling is not satisfactory, sedimentation centrifuges should be considered. Centrifuging will give a cleaner separation than that obtainable by gravity settling. Centrifuges can be used where the difference in gravity between the liquids is very small, as low as  $100 \text{ kg/m}^3$ , and they can handle high throughputs, up to around  $100 \text{ m}^3/\text{h}$ . Also, centrifuging will usually break any emulsion that may form. Bowl or disc centrifuges are normally used (see Section 10.4.3).

### *Hydrocyclones*

Hydrocyclones are used for some liquid-liquid separations, but are not so effective in this application as in separating solids from liquids.

## 10.7. SEPARATION OF DISSOLVED LIQUIDS

The most commonly used techniques for the separation and purification of miscible liquids are distillation and solvent extraction. In recent years, adsorption, ion exchange and chromatography have become practical alternatives to distillation or solvent extraction in many special applications.

Distillation is probably the most widely used separation technique in the chemical process industries, and is covered in Chapter 11 of this volume, and Chapter 11 of Volume 2. Solvent extraction and the associated technique, leaching (solid-liquid extraction) are covered in Volume 2, Chapters 13 and 10. Adsorption, which can be used for the separation of liquid and gases mixtures, is covered in Chapter 17 of Volume 2. Adsorption is also covered in the books by Suzuki (1990) and Crittenden and Thomas (1998).

Ion exchange, the separation of dissolved solids, is covered in Chapter 18 of Volume 2. Through ion exchange is usually associated with water purification the technique has applications in other industries.

Chromatography, which is finding increasing applications in the downstream processing of biochemical products, is covered in Chapter 19 of Volume 2.

In this section, the discussion is restricted to a brief review of solvent-extraction processes.

### 10.7.1. Solvent extraction and leaching

#### ***Solvent extraction (liquid–liquid extraction)***

Solvent extraction, also called liquid–liquid extraction, can be used to separate a substance from a solution by extraction into another solvent. It can be used either to recover a valuable substance from the original solution, or to purify the original solvent by removing an unwanted component. Examples of solvent extraction are: the extraction of uranium and plutonium salts from solution in nitric acid, in the nuclear industry; and the purification of water.

The process depends on the substance being extracted, the solute, having a greater solubility in the solvent used for the extraction than in the original feed solvent. The two solvents must be essentially immiscible.

The solvents are mixed in a contactor, to effect the transfer of solute, and then the phases separated. The depleted feed solvent leaving the extractor is called the raffinate, and the solute rich extraction solvent, the extract. The solute is normally recovered from the extraction solvent, by distillation, and the extraction solvent recycled.

The simplest form of extractor is a mixer-settler, which consist of an agitated tank and a decanter.

The design of extraction columns is discussed in Chapter 11, Section 11.16. See also, Volume 2, Chapter 13, Walas (1990) and Perry *et al.* (1997).

#### ***Leaching***

Liquids can be extracted from solids by leaching. As the name implies, the soluble liquid contained in a solid is leached out by contacting the solid with a suitable solvent. A principal application of leaching is in the extraction of valuable oils from nuts and seeds; such as, palm oil and rape seed oil.

The equipment used to contact the solids with the solvent is usually a special designs to suit the type of solid being processed, and is to an extent unique to the particular industry. General details of leaching equipment are given in Volume 2, Chapter 10 and in Perry *et al.* (1997).

The leaching is normally done using a number of stages. In this respect, the process is similar to liquid–liquid extraction, and the methods used to determine the number of stages required are similar.

For a detailed discussion of the procedures used to determine the number of stages required for a particular process, see Volume 2, Chapter 10 or Prabhudesai (1997).



## 10.8. GAS-SOLIDS SEPARATIONS (GAS CLEANING)

The primary need for gas-solid separation processes is for gas cleaning: the removal of dispersed finely divided solids (dust) and liquid mists from gas streams. Process gas streams must often be cleaned up to prevent contamination of catalysts or products, and to avoid damage to equipment, such as compressors. Also, effluent gas streams must be cleaned to comply with air-pollution regulations and for reasons of hygiene, to remove toxic and other hazardous materials; see IChemE (1992).

There is also often a need for clean, filtered, air for process using air as a raw material, and where clean working atmospheres are needed: for instance, in the pharmaceutical and electronics industries.

The particles to be removed may range in size from large molecules, measuring a few hundredths of a micrometre, to the coarse dusts arising from the attrition of catalysts or the fly ash from the combustion of pulverised fuels.

A variety of equipment has been developed for gas cleaning. The principal types used in the process industries are listed in Table 10.11, which is adapted from a selection guide given by Sargent (1971). Table 10.11 shows the general field of application of each type in terms of the particle size separated, the expected separation efficiency, and the throughput. It can be used to make a preliminary selection of the type of equipment likely to be suitable for a particular application. Descriptions of the equipment shown in Table 10.11 can be found in various handbooks: Perry *et al.* (1997), Schweitzer (1997); and in specialist texts: Strauss (1975). Gas cleaning is also covered in Volume 2, Chapter 1.

Gas-cleaning equipment can be classified according to the mechanism employed to separate the particles: gravity settling, impingement, centrifugal force, filtering, washing and electrostatic precipitation.

### 10.8.1. Gravity settlers (settling chambers)

Settling chambers are the simplest form of industrial gas-cleaning equipment, but have only a limited use; they are suitable for coarse dusts, particles larger than 50  $\mu\text{m}$ . They are essentially long, horizontal, rectangular chambers; through which the gas flows. The solids settle under gravity and are removed from the bottom of the chamber. Horizontal plates or vertical baffles are used in some designs to improve the separation. Settling chambers offer little resistance to the gas flow, and can be designed for operation at high temperature and high pressure, and for use in corrosive atmospheres.

The length of chamber required to settle a given particle size can be estimated from the settling velocity (calculated using Stokes' law) and the gas velocity. A design procedure is given by Jacob and Dhodapkar (1997).

### 10.8.2. Impingement separators

Impingement separators employ baffles to achieve the separation. The gas stream flows easily round the baffles, whereas the solid particles, due to their higher momentum, tend to continue in their line of flight, strike the baffles and are collected. A variety of baffle

Table 10.11. Gas-cleaning equipment

Type of equipment	Minimum particle size ( $\mu\text{m}$ )	Minimum loading ( $\text{mg}/\text{m}^3$ )	Approx. efficiency (%)	Typical gas velocity (m/s)	Maximum capacity ( $\text{m}^3/\text{s}$ )	Gas pressure drop (mm $\text{H}_2\text{O}$ )	Liquid rate ( $\text{m}^3/10^3 \text{ m}^3 \text{ gas}$ )	Space required (relative)
<i>Dry collectors</i>								
Settling chamber	50	12,000	50	1.5–3	none	5	—	Large
Baffle chamber	50	12,000	50	5–10	none	3–12	—	Medium
Louver	20	2500	80	10–20	15	10–50	—	Small
Cyclone	10	2500	85	10–20	25	10–70	—	Medium
Multiple cyclone	5	2500	95	10–20	100	50–150	—	Small
Impingement	10	2500	90	15–30	none	25–50	—	Small
<i>Wet scrubbers</i>								
Gravity spray	10	2500	70	0.5–1	50	25	0.05–0.3	Medium
Centrifugal	5	2500	90	10–20	50	50–150	0.1–1.0	Medium
Impingement	5	2500	95	15–30	50	50–200	0.1–0.7	Medium
Packed	5	250	90	0.5–1	25	25–250	0.7–2.0	Medium
Jet	0.5 to 5 (range)	250	90	10–100	50	none	7–14	Small
Venturi	0.5	250	99	50–200	50	250–750	0.4–1.4	Small
<i>Others</i>								
Fabric filters	0.2	250	99	0.01–0.1	100	50–150	—	Large
Electrostatic precipitators	2	250	99	5–30	1000	5–25	—	Large

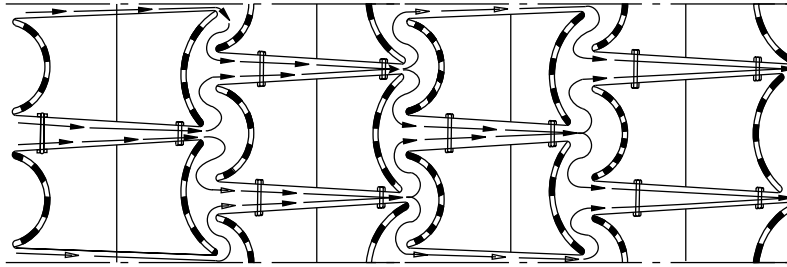


Figure 10.42. Impingement separator (section showing gas flow)

designs is used in commercial equipment; a typical example is shown in Figure 10.42. Impingement separators cause a higher pressure drop than settling chambers, but are capable of separating smaller particle sizes, 10–20  $\mu\text{m}$ .

### 10.8.3. Centrifugal separators (cyclones)

Cyclones are the principal type of gas-solids separator employing centrifugal force, and are widely used. They are basically simple constructions; can be made from a wide range of materials; and can be designed for high temperature and pressure operation.

Cyclones are suitable for separating particles above about 5  $\mu\text{m}$  diameter; smaller particles, down to about 0.5  $\mu\text{m}$ , can be separated where agglomeration occurs.

The most commonly used design is the reverse-flow cyclone, Figure 10.43; other configurations are used for special purposes. In a reverse-flow cyclone the gas enters the top chamber tangentially and spirals down to the apex of the conical section; it then moves upward in a second, smaller diameter, spiral, and exits at the top through a central vertical pipe. The solids move radially to the walls, slide down the walls, and are collected at the bottom. Design procedures for cyclones are given by Constantinescu (1984). Strauss (1975), Koch and Licht (1977) and Stairmand (1951). The theoretical concepts and experimental work on which the design methods are based on discussed in Volume 2, Chapter 8. Stairmand's method is outlined below and illustrated in Example 10.4.

#### **Cyclone design**

Stairmand developed two standard designs for gas-solid cyclones: a high-efficiency cyclone, Figure 10.44a, and a high throughput design, Figure 10.44b. The performance curves for these designs, obtained experimentally under standard test conditions, are shown in Figures 10.45a and 10.45b. These curves can be transformed to other cyclone sizes and operating conditions by use of the following scaling equation, for a given separating efficiency:

$$d_2 = d_1 \left[ \left( \frac{D_{c2}}{D_{c1}} \right)^3 \times \frac{Q_1}{Q_2} \times \frac{\Delta\rho_1}{\Delta\rho_2} \times \frac{\mu_2}{\mu_1} \right]^{1/2} \quad (10.8)$$

where  $d_1$  = mean diameter of particle separated at the standard conditions, at the chosen separating efficiency, Figures 10.45a or 10.45b,

$d_2$  = mean diameter of the particle separated in the proposed design, at the same separating efficiency,

$D_{c1}$  = diameter of the standard cyclone = 8 inches (203 mm),

$D_{c2}$  = diameter of proposed cyclone, mm,

$Q_1$  = standard flow rate:

for high efficiency design = 223 m<sup>3</sup>/h,

for high throughput design = 669 m<sup>3</sup>/h,

$Q_2$  = proposed flow rate, m<sup>3</sup>/h,

$\Delta\rho_1$  = solid-fluid density difference in standard conditions = 2000 kg/m<sup>3</sup>,

$\Delta\rho_2$  = density difference, proposed design,

$\mu_1$  = test fluid viscosity (air at 1 atm, 20°C)

= 0.018 mN s/m<sup>2</sup>,

$\mu_2$  = viscosity, proposed fluid.

A performance curve for the proposed design can be drawn up from Figures 10.45a or 10.45b by multiplying the grade diameter at, say, each 10 per cent increment of efficiency, by the scaling factor given by equation 10.8; as shown in Figure 10.46 (p. 453).

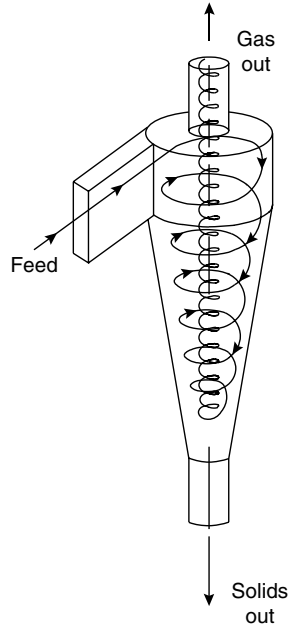


Figure 10.43. Reverse-flow cyclone

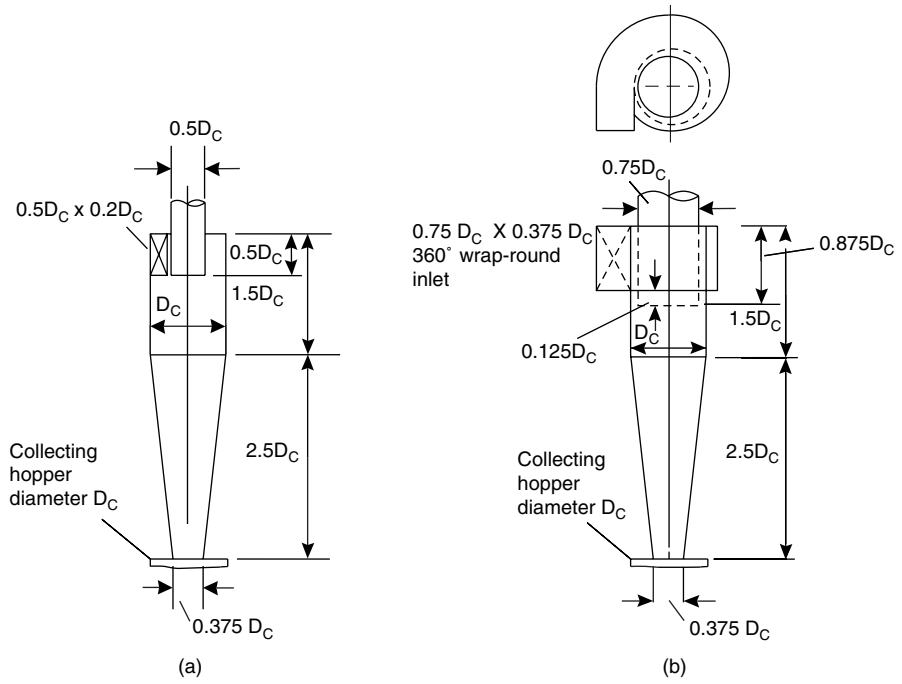


Figure 10.44. Standard cyclone dimension (a) High efficiency cyclone (b) High gas rate cyclone

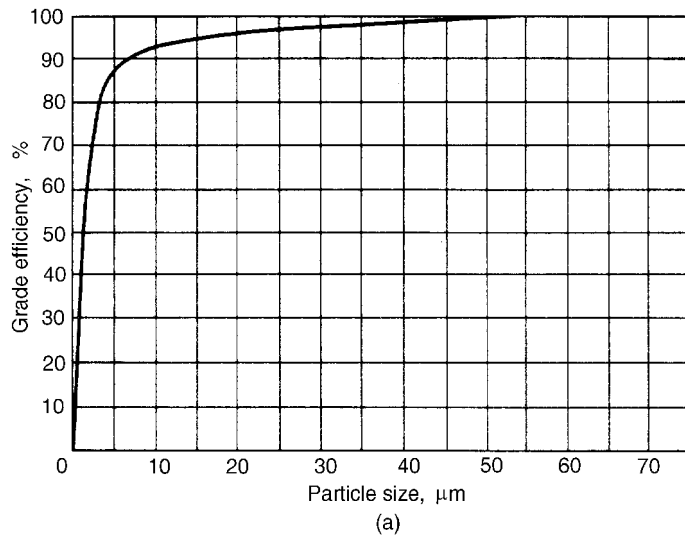


Figure 10.45. Performance curves, standard conditions (a) High efficiency cyclone

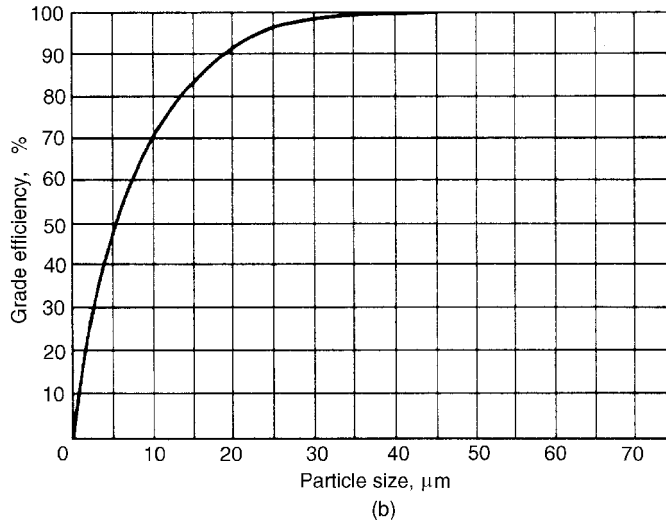


Figure 10.45 (continued). Performance curves, standard conditions (b) High gas rate cyclone

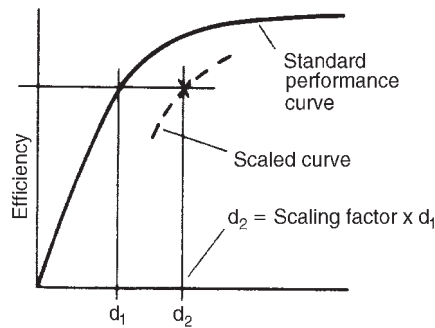


Figure 10.46. Scaled performance curve

An alternative method of using the scaling factor, that does not require redrawing the performance curve, is used in Example 10.4. The cyclone should be designed to give an inlet velocity of between 9 and 27 m/s (30 to 90 ft/s); the optimum inlet velocity has been found to be 15 m/s (50 ft/s).

### Pressure drop

The pressure drop in a cyclone will be due to the entry and exit losses, and friction and kinetic energy losses in the cyclone. The empirical equation given by Stairmand (1949) can be used to estimate the pressure drop:

$$\Delta P = \frac{\rho_f}{203} \left\{ u_1^2 \left[ 1 + 2\phi^2 \left( \frac{2r_t}{r_e} - 1 \right) \right] + 2u_2^2 \right\} \quad (10.9)$$

where  $\Delta P$  = cyclone pressure drop, millibars,

$\rho_f$  = gas density, kg/m<sup>3</sup>,

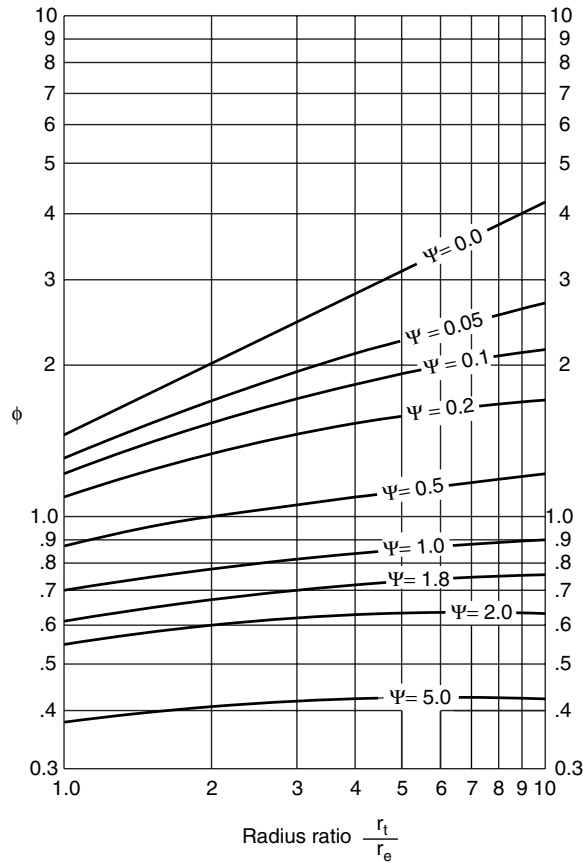


Figure 10.47. Cyclone pressure drop factor

$u_1$  = inlet duct velocity, m/s,

$u_2$  = exit duct velocity, m/s,

$r_t$  = radius of circle to which the centre line of the inlet is tangential, m,

$r_e$  = radius of exit pipe, m,

$\phi$  = factor from Figure 10.47,

$\psi$  = parameter in Figure 10.47, given by:

$$\psi = f_c \frac{A_s}{A_1}$$

$f_c$  = friction factor, taken as 0.005 for gases,

$A_s$  = surface area of cyclone exposed to the spinning fluid, m<sup>2</sup>.

For design purposes this can be taken as equal to the surface area of a cylinder with the same diameter as the cyclone and length equal to the total height of the cyclone (barrel plus cone).

$A_1$  = area of inlet duct, m<sup>2</sup>.

Stairmand's equation is for the gas flowing alone, containing no solids. The presence of solids will normally increase the pressure drop over that calculated using equation 10.9, depending on the solids loading. Alternative design methods for cyclones, which include procedures for estimating the true pressure drop, are given by Perry *et al.* (1997) and Yang (1999); see also Zenz (2001).

### General design procedure

1. Select either the high-efficiency or high-throughput design, depending on the performance required.
2. Obtain an estimate of the particle size distribution of the solids in the stream to be treated.
3. Estimate the number of cyclones needed in parallel.
4. Calculate the cyclone diameter for an inlet velocity of 15 m/s (50 ft/s). Scale the other cyclone dimensions from Figures 10.44a or 10.44b.
5. Calculate the scale-up factor for the transposition of Figures 10.45a or 10.45b.
6. Calculate the cyclone performance and overall efficiency (recovery of solids). If unsatisfactory try a smaller diameter.
7. Calculate the cyclone pressure drop and, if required, select a suitable blower.
8. Cost the system and optimise to make the best use of the pressure drop available, or, if a blower is required, to give the lowest operating cost.

### Example 10.4

Design a cyclone to recover solids from a process gas stream. The anticipated particle size distribution in the inlet gas is given below. The density of the particles is 2500 kg/m<sup>3</sup>, and the gas is essentially nitrogen at 150°C. The stream volumetric flow-rate is 4000 m<sup>3</sup>/h, and the operation is at atmospheric pressure. An 80 per cent recovery of the solids is required.

Particle size ( $\mu\text{m}$ )	50	40	30	20	10	5	2
Percentage by weight less than	90	75	65	55	30	10	4

### Solution

As 30 per cent of the particles are below 10  $\mu\text{m}$  the high-efficiency design will be required to give the specified recovery.

$$\text{Flow-rate} = \frac{4000}{3600} = 1.11 \text{ m}^3/\text{s}$$

$$\text{Area of inlet duct, at 15 m/s} = \frac{1.11}{15} = 0.07 \text{ m}^2$$

From Figure 10.44a, duct area = 0.5  $D_c \times 0.2 D_c$

$$\text{so, } D_c = 0.84$$

This is clearly too large compared with the standard design diameter of 0.203 m.



Try four cyclones in parallel,  $D_c = 0.42$  m.

$$\text{Flow-rate per cyclone} = 1000 \text{ m}^3/\text{h}$$

$$\text{Density of gas at } 150^\circ\text{C} = \frac{28}{22.4} \times \frac{273}{423} = 0.81 \text{ kg/m}^2,$$

negligible compared with the solids density

$$\text{Viscosity of } \text{N}_2 \text{ at } 150^\circ\text{C} = 0.023 \text{ cp(mN s/m}^2)$$

From equation 10.8,

$$\text{scaling factor} = \left[ \left( \frac{0.42}{0.203} \right)^3 \times \frac{223}{1000} \times \frac{2000}{2500} \times \frac{0.023}{0.018} \right]^{1/2} = \underline{\underline{1.42}}$$

The performance calculations, using this scaling factor and Figure 10.45a, are set out in the table below:

*Calculated performance of cyclone design, Example 10.4*

1	2	3	4	5	6	7
Particle size ( $\mu\text{m}$ )	Per cent in range	Mean particle size $\div$ scaling factor	Efficiency at scaled size % (Figure 10.46a)	Collected $\frac{(2) \times (4)}{100}$	Grading at exit $(2)-(5)$	Per cent at exit
>50	10	35	98	9.8	0.2	1.8
50-40	15	32	97	14.6	0.4	3.5
40-30	10	25	96	9.6	0.4	3.5
30-20	10	18	95	9.5	0.5	4.4
20-10	25	11	93	23.3	1.7	15.1
10-5	20	5	86	17.2	2.8	24.8
5-2	6	3	72	4.3	1.7	15.1
2-0	4	1	10	0.4	3.6	31.8
	100		Overall collection efficiency	<u>88.7</u>	11.3	100.0

The collection efficiencies shown in column 4 of the table were read from Figure 10.45a at the scaled particle size, column 3. The overall collection efficiency satisfies the specified solids recovery. The proposed design with dimension in the proportions given in Figure 10.44a is shown in Figure 10.48.

### **Pressure-drop calculation**

$$\text{Area of inlet duct, } A_1, = 210 \times 80 = 16,800 \text{ mm}^2$$

$$\begin{aligned} \text{Cyclone surface area, } A_s &= \pi 420 \times (630 + 1050) \\ &= 2.218 \times 10^6 \text{ mm}^2 \end{aligned}$$

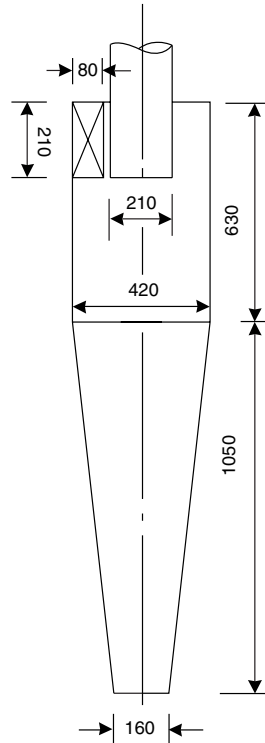


Figure 10.48. Proposed cyclone design, all dimensions mm (Example 10.4)

$f_c$  taken as 0.005

$$\psi = \frac{f_c A_s}{A_1} = \frac{0.005 \times 2.218 \times 10^6}{16,800} = 0.66$$

$$\frac{r_t}{r_e} = \frac{(420 - (80/2))}{210} = 1.81$$

From Figure 10.47,  $\phi = 0.9$ .

$$u_1 = \frac{1000}{3600} \times \frac{10^6}{16,800} = 16.5 \text{ m/s}$$

$$\text{Area of exit pipe} = \frac{\pi \times 210^2}{4} = 34,636 \text{ mm}^2$$

$$u_2 = \frac{1000}{3600} \times \frac{10^6}{34,636} = 8.0 \text{ m/s}$$

From equation 10.6

$$\begin{aligned} \Delta P &= \frac{0.81}{203} [16.5^2 [1 + 2 \times 0.9^2 (2 \times 1.81 - 1)] + 2 \times 8.0^2] \\ &= \underline{\underline{6.4 \text{ millibar}}} \quad (67 \text{ mm H}_2\text{O}) \end{aligned}$$

This pressure drop looks reasonable.

### 10.8.4. Filters

The filters used for gas cleaning separate the solid particles by a combination of impingement and filtration; the pore sizes in the filter media used are too large simply to filter out the particles. The separating action relies on the precoating of the filter medium by the first particles separated; which are separated by impingement on the filter medium fibres. Woven or felted cloths of cotton and various synthetic fibres are commonly used as the filter media. Glass-fibre mats and paper filter elements are also used.

A typical example of this type of separator is the bag filter, which consists of a number of bags supported on a frame and housed in a large rectangular chamber, Figure 10.49. The deposited solids are removed by mechanically vibrating the bag, or by periodically reversing the gas flow. Bag filters can be used to separate small particles, down to around  $1\ \mu\text{m}$ , with a high separating efficiency. Commercial units are available to suit most applications and should be selected in consultation with the vendors.

The design and specification of bag filters (baghouses) is covered by Kraus (1979).

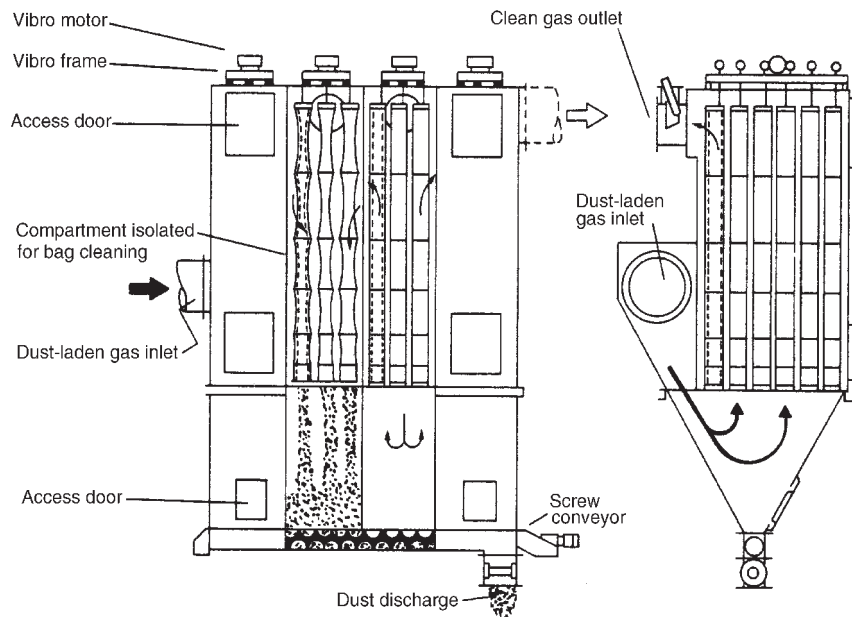


Figure 10.49. Multi-compartment vibro bag filter

### ***Air filters***

Dust-free air is required for many process applications. The requirements of air filtration differ from those of process gas filtration mainly in that the quantity of dust to be removed will be lower, typically less than  $10\ \text{mg}/\text{m}^3$  ( $\sim 5$  grains per  $1000\ \text{ft}^3$ ); and also in that there is no requirement to recover the material collected.

Three basic types of air filter are used: viscous, dry and continuous. Viscous and dry units are similar in construction, but the filter medium of the viscous type is coated with a viscous material, such as a mineral oil, to retain the dust. The filters are made up from standard, preformed, sections, supported on a frame in a filter housing. The sections are removed periodically for cleaning or replacement. Various designs of continuous filtration equipment are also available, employing either viscous or dry filter elements, but in which the filter is cleaned continuously. A comprehensive description of air-filtration equipment is given by Strauss (1975).

### 10.8.5. Wet scrubbers (washing)

In wet scrubbing the dust is removed by counter-current washing with a liquid, usually water, and the solids are removed as a slurry. The principal mechanism involved is the impact (impingement) of the dust particles and the water droplets. Particle sizes down to  $0.5 \mu\text{m}$  can be removed in suitably designed scrubbers. In addition to removing solids, wet scrubbers can be used to simultaneously cool the gas and neutralise any corrosive constituents.

Spray towers, and plate and packed columns are used, as well as a variety of proprietary designs. Spray towers have a low pressure drop but are not suitable for removing very fine particles, below  $10 \mu\text{m}$ . The collecting efficiency can be improved by the use of plates or packing but at the expense of a higher pressure drop.

Venturi and orifice scrubbers are simple forms of wet scrubbers. The turbulence created by the venturi or orifice is used to atomise water sprays and promote contact between the liquid droplets and dust particles. The agglomerated particles of dust and liquid are then collected in a centrifugal separator, usually a cyclone.

### 10.8.6. Electrostatic precipitators

Electrostatic precipitators are capable of collecting very fine particles,  $<2 \mu\text{m}$ , at high efficiencies. However, their capital and operating costs are high, and electrostatic precipitation should only be considered in place of alternative processes, such as filtration, where the gases are hot or corrosive. Electrostatic precipitators are used extensively in the metallurgical, cement and electrical power industries. Their main application is probably in the removal of the fine fly ash formed in the combustion of pulverised coal in powerstation boilers. The basic principle of operation is simple. The gas is ionised in passing between a high-voltage electrode and an earthed (grounded) electrode; the dust particles become charged and are attracted to the earthed electrode. The precipitated dust is removed from the electrodes mechanically, usually by vibration, or by washing. Wires are normally used for the high-voltage electrode, and plates or tubes for the earthed electrode. A typical design is shown in Figure 10.50. A full description of the construction, design and application of electrostatic precipitators is given by Schneider *et al.* (1975) and Parker (2002).

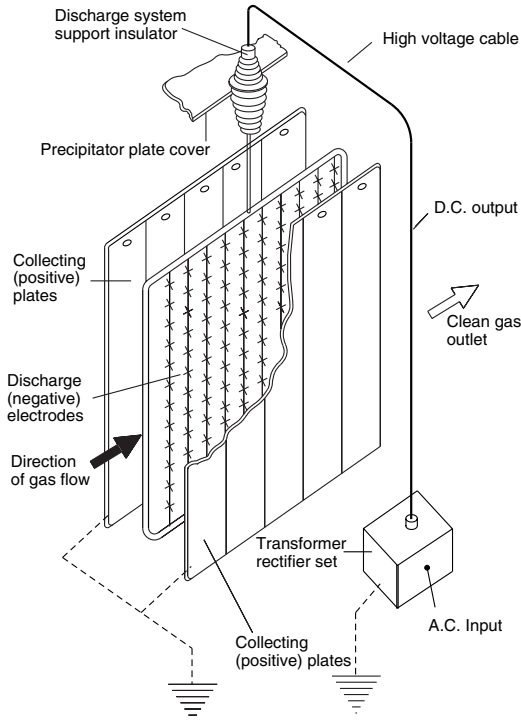


Figure 10.50. Electrostatic precipitator

## 10.9. GAS-LIQUID SEPARATORS

The separation of liquid droplets and mists from gas or vapour streams is analogous to the separation of solid particles and, with the possible exception of filtration, the same techniques and equipment can be used.

Where the carryover of some fine droplets can be tolerated it is often sufficient to rely on gravity settling in a vertical or horizontal separating vessel (knockout pot).

Knitted mesh demisting pads are frequently used to improve the performance of separating vessels where the droplets are likely to be small, down to  $1\ \mu\text{m}$ , and where high separating efficiencies are required. Proprietary demister pads are available in a wide range of materials, metals and plastics; thickness and pad densities. For liquid separators, stainless steel pads around 100 mm thick and with a nominal density of  $150\ \text{kg/m}^3$  would generally be used. Use of a mister pad allows a smaller vessel to be used. Separating efficiencies above 99% can be obtained with low pressure drop. The design and specification of demister pads for gas-liquid separators is discussed by Pryce Bailey and Davies (1973).

The design methods for horizontal separators given below are based on a procedure given by Gerunda (1981).

Cyclone separators are also frequently used for gas-liquid separation. They can be designed using the same methods for gas-solids cyclones. The inlet velocity should be kept below 30 m/s to avoid pick-up of liquid from the cyclone surfaces.

### 10.9.1. Settling velocity

Equation 10.10 can be used to estimate the settling velocity of the liquid droplets, for the design of separating vessels.

$$u_t = 0.07[(\rho_L - \rho_v)/\rho_v]^{1/2} \quad (10.10)$$

where  $u_t$  = settling velocity, m/s,

$\rho_L$  = liquid density, kg/m<sup>3</sup>,

$\rho_v$  = vapour density, kg/m<sup>3</sup>.

If a demister pad is not used, the value of  $u_t$  obtained from equation 10.10 should be multiplied by a factor of 0.15 to provide a margin of safety and to allow for flow surges.

### 10.9.2. Vertical separators

The layout and typical proportions of a vertical liquid–gas separator are shown in Figure 10.51a.

The diameter of the vessel must be large enough to slow the gas down to below the velocity at which the particles will settle out. So the minimum allowable diameter will

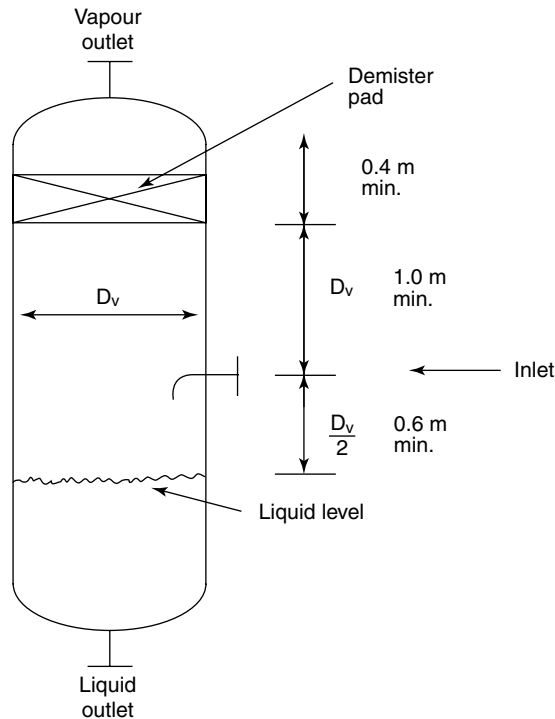


Figure 10.51a. Vertical liquid-vapour separator

be given by:

$$D_v = \sqrt{\left(\frac{4V_v}{\pi u_s}\right)} \quad (10.11)$$

where  $D_v$  = minimum vessel diameter, m,

$V_v$  = gas, or vapour volumetric flow-rate, m<sup>3</sup>/s,

$u_s = u_t$ , if a demister pad is used, and  $0.15 u_t$  for a separator without a demister pad;  $u_t$  from equation (10.10), m/s.

The height of the vessel outlet above the gas inlet should be sufficient to allow for disengagement of the liquid drops. A height equal to the diameter of the vessel or 1 m, which ever is the greatest, should be used, see Figure 10.51*a*.

The liquid level will depend on the hold-up time necessary for smooth operation and control; typically 10 minutes would be allowed.

### Example 10.5

Make a preliminary design for a separator to separate a mixture of steam and water; flow-rates: steam 2000 kg/h, water 1000 kg/h; operating pressure 4 bar.

### Solution

From steam tables, at 4 bar: saturation temperature 143.6°C, liquid density 926.4 kg/m<sup>3</sup>, vapour density 2.16 kg/m<sup>3</sup>.

$$u_t = 0.07[(926.4 - 2.16)/2.16]^{\frac{1}{2}} = 1.45 \text{ m/s} \quad (10.10)$$

As the separation of condensate from steam is unlikely to be critical, a demister pad will not be specified.

So,  $u_t = 0.15 \times 1.45 = 0.218 \text{ m/s}$

$$\text{Vapour volumetric flow-rate} = \frac{2000}{3600 \times 2.16} = 0.257 \text{ m}^3/\text{s}$$

$$D_v = \sqrt{[(4 \times 0.257)/(\pi \times 0.218)]} = 1.23 \text{ m, round to 1.25 m (4 ft).} \quad (10.11)$$

$$\text{Liquid volumetric flow-rate} = \frac{1000}{3600 \times 926.14} = 3.0 \times 10^{-4} \text{ m}^3/\text{s}$$

Allow a minimum of 10 minutes hold-up.

$$\text{Volume held in vessel} = 3.0 \times 10^{-4} \times (10 \times 60) = 0.18 \text{ m}^3$$

$$\begin{aligned} \text{Liquid depth required, } h_v &= \frac{\text{volume held-up}}{\text{vessel cross-sectional area}} \\ &= \frac{0.18}{(\pi \times 1.25^2/4)} = 0.15 \text{ m} \end{aligned}$$

Increase to 0.3 m to allow space for positioning the level controller.

### 10.9.3. Horizontal separators

The layout of a typical horizontal separator is shown in Figure 10.51*b*.

A horizontal separator would be selected when a long liquid hold-up time is required.

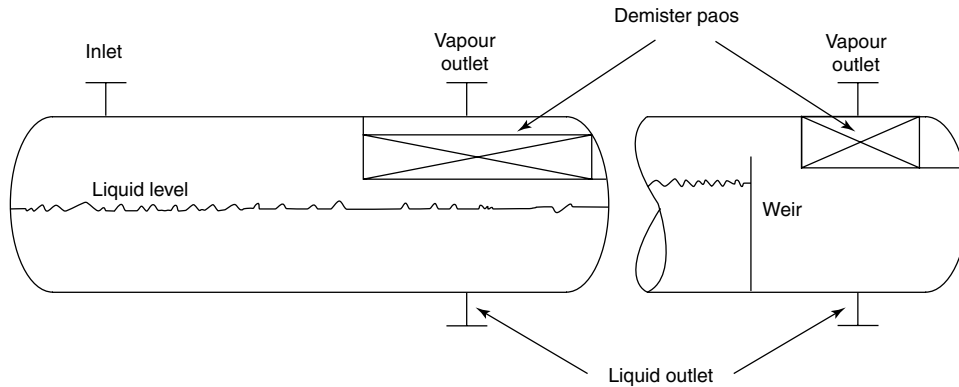


Figure 10.51*b*. Horizontal liquid vapour separator

In the design of a horizontal separator the vessel diameter cannot be determined independently of its length, unlike for a vertical separator. The diameter and length, and the liquid level, must be chosen to give sufficient vapour residence time for the liquid droplets to settle out, and for the required liquid hold-up time to be met.

The most economical length to diameter ratio will depend on the operating pressure (see Chapter 13). As a general guide the following values can be used:

Operating pressure, bar	Length: diameter, $L_v/D_v$
0–20	3
20–35	4
>35	5

The relationship between the area for vapour flow,  $A_v$ , and the height above the liquid level,  $h_v$ , can be found from tables giving the dimensions of the segments of circles; see Perry and Green (1984), or from Figure 11.32 and 11.33 in Chapter 11.

For preliminary designs, set the liquid height at half the vessel diameter,

$$h_v = D_v/2 \text{ and } f_v = 0.5,$$

where  $f_v$  is the fraction of the total cross-sectional area occupied by the vapour.

The design procedure for horizontal separators is illustrated in the following example, example 10.6.

#### Example 10.6

Design a horizontal separator to separate 10,000 kg/h of liquid, density 962.0 kg/m<sup>3</sup>, from 12,500 kg/h of vapour, density 23.6 kg/m<sup>3</sup>. The vessel operating pressure will be 21 bar.



**Solution**

$$u_t = 0.07[(962.0 - 23.6)/23.6]^{1/2} = 0.44 \text{ m/s}$$

Try a separator without a demister pad.

$$u_a = 0.15 \times 0.44 = 0.066 \text{ m/s}$$

$$\text{Vapour volumetric flow-rate} = \frac{12,500}{3600 \times 23.6} = 0.147 \text{ m}^3/\text{s}$$

Take  $h_v = 0.5D_v$  and  $L_v/D_v = 4$

$$\text{Cross-sectional area for vapour flow} = \frac{\pi D_v^2}{4} \times 0.5 = 0.393D_v^2$$

$$\text{Vapour velocity, } u_v = \frac{0.147}{0.393D_v^2} = 0.374D_v^{-2}$$

Vapour residence time required for the droplets to settle to liquid surface

$$= h_v/u_a = 0.5D_v/0.066 = 7.58D_v$$

Actual residence time = vessel length/vapour velocity

$$= L_v/u_v = \frac{4D_v}{0.374 D_v^{-2}} = 10.70D_v^3$$

For satisfactory separation required residence time = actual.

$$\text{So, } 7.58D_v = 10.70D_v^3$$

$$D_v = 0.84 \text{ m, say } 0.92 \text{ m (3 ft, standard pipe size)}$$

Liquid hold-up time,

$$\text{liquid volumetric flow-rate} = \frac{10,000}{3600 \times 962.0} = 0.00289 \text{ m}^3/\text{s}$$

$$\text{liquid cross-sectional area} = \frac{\pi \times 0.92^2}{4} \times 0.5 = 0.332 \text{ m}^2$$

Length,  $L_v = 4 \times 0.92 = 3.7 \text{ m}$

$$\text{Hold-up volume} = 0.332 \times 3.7 = 1.23 \text{ m}^3$$

Hold-up time = liquid volume/liquid flow-rate

$$= 1.23/0.00289 = 426 \text{ s} = 7 \text{ minutes.}$$

This is unsatisfactory, 10 minutes minimum required.

Need to increase the liquid volume. This is best done by increasing the vessel diameter. If the liquid height is kept at half the vessel diameter, the diameter must be increased by a factor of roughly  $(10/7)^{0.5} = 1.2$ .

$$\text{New } D_v = 0.92 \times 1.2 = 1.1 \text{ m}$$



Table 10.13. Selection of comminution equipment for various materials (after Marshall, 1974) Note: Moh's scale of hardness is given in Table 10.12

Material class no	Material classification	Typical materials in class	Suitable equipment for product size classes			Remarks
			Down to 5 mesh	Between 5 and 300 mesh	Less than 300 mesh	
1	Hard and tough	Mica Scrap and powdered metals	Jaw crushers Gyratory crushers Cone crushers Autogeneous mills	Ball, pebble, rod and cone mills Tube mills Vibration mills	Ball, pebble and cone mills Tube mills Vibration and vibro-energy mills Fluid-energy mills	Moh's hardness 5-10, but includes other tough materials of lower hardness
2	Hard, abrasive and brittle	Coke, quartz, granite	Jaw crushers Gyratory and cone crushers Roll crushers	Ball, pebble, rod and cone mills Vibration mills Roller mills	Ball, pebble and cone mills Tube mills Vibration and vibro-energy mills Fluid-energy mills	Moh's hardness 5-10 High wear rate/ contamination in high-speed machinery Use machines with abrasion resistant linings
3	Intermediate hard, and friable	Barytes, fluor-spar, limestone	Jaw crushers Gyratory crushers Roll crushers Edge runner mills Impact breakers Autogeneous mills Cone crushers	Ball, pebble, rod and cone mills Tube mills Ring roll mills Ring ball mills Roller mills Peg and disc mills Cage mills Impact breakers Vibration mills	Ball, pebble and cone mills Tube mills Perl mills Vibration and vibro-energy mills Fluid-energy mills	Moh's hardness 3-5

4	Fibrous, low abrasion and possibly tough	Wood, asbestos	Cone crushers Roll crushers Edge runner mills Autogeneous mills Impact breakers	Ball, pebble, rod and cone mills Tube mills Roller mills Peg and disc mills Cage mills Impact breakers Vibration mills Rotary cutters and dicers	Ball, pebble and cone mills Tube mills Sand mills Perl mills Vibration and vibro-energy mills Colloid mills	Wide range of hardness Low-temperature, liquid nitrogen, useful to embrittle soft but tough materials
5	Soft and friable	Sulphur, gypsum rock salt	Cone crushers Roll crushers Edge runner mills Impact breakers Autogeneous mills	Ball, pebble and cone mills Tube mills Ring roll mills Ring ball mills Roller mills Peg and disc mills Cage mills Impact breakers Vibration mills	Ball, pebble and cone mills Tube mills Sand mills Perl mills Vibration and vibro-energy mills Colloid mills Fluid-energy mills Peg and disc mills	Moh's hardness 1-3
6	Sticky	Clays, certain organic pigments	Roll crushers Impact breakers Edge runner mills	Ball, pebble, rod and cone mills* Tube mills* Peg and disc mills Cage mills Ring roll mills	Ball, pebble and cone mills* Tube mills* Sand mills Perl mills Vibration and vibro-energy mills Colloid mills	Wide range of Moh's hardness although mainly less than 3 Tends to clog *Wet grinding employed except for certain exceptional cases

\*All ball, pebble, rod and cone mills, edge runner mills, tube mills, vibration mills and some ring ball mills may be used wet or dry except where stated. The perl mills, sand mills and colloid mills may be used for wet milling only.

The main factors to be considered when selecting equipment for crushing and grinding are:

1. The size of the feed.
2. The size reduction ratio.
3. The required particle size distribution of the product.
4. The throughput.
5. The properties of the material: hardness, abrasiveness, stickiness, density, toxicity, flammability.
6. Whether wet grinding is permissible.

The selection guides given by Lowrison (1974) and Marshall (1974), which are reproduced in Tables 10.12 (see p. 465) and 10.13, can be used to make a preliminary selection based on particle size and material hardness. Descriptions of most of the equipment listed in these tables are given in Volume 2, Chapter 2; or can be found in the literature; Perry *et al.* (1997), Hiorns (1970), Lowrison (1974). The most commonly used equipment for coarse size reduction are jaw crushers and rotary crushers; and for grinding, ball mills or their variants: pebble, roll and tube mills.

## 10.11. MIXING EQUIPMENT

The preparation of mixtures of solids, liquids and gases is an essential part of most production processes in the chemical and allied industries; covering all processing stages, from the preparation of reagents through to the final blending of products. The equipment used depends on the nature of the materials and the degree of mixing required. Mixing is often associated with other operations, such as reaction and heat transfer. Liquid and solids mixing operations are frequently carried out as batch processes.

In this section, mixing processes will be considered under three separate headings: gases, liquids and solids.

### 10.11.1. Gas mixing

Specialised equipment is seldom needed for mixing gases, which because of their low viscosities mix easily. The mixing given by turbulent flow in a length of pipe is usually sufficient for most purposes. Turbulence promoters, such as orifices or baffles, can be used to increase the rate of mixing. The piping arrangements used for inline mixing are discussed in the section on liquid mixing.

### 10.11.2. Liquid mixing

The following factors must be taken into account when choosing equipment for mixing liquids:

1. Batch or continuous operation.
2. Nature of the process: miscible liquids, preparation of solutions, or dispersion of immiscible liquids.
3. Degree of mixing required.
4. Physical properties of the liquids, particularly the viscosity.
5. Whether the mixing is associated with other operations: reaction, heat transfer.

For the continuous mixing of low viscosity fluids inline mixers can be used. For other mixing operations stirred vessels or proprietary mixing equipment will be required.

### ***Inline mixing***

Static devices which promote turbulent mixing in pipelines provide an inexpensive way of continuously mixing fluids. Some typical designs are shown in Figures 10.52a, b, c. A simple mixing tee, Figure 10.52a, followed by a length of pipe equal to 10 to 20 pipe diameters, is suitable for mixing low viscosity fluids ( $\leq 50 \text{ mN s/m}^2$ ) providing the flow is turbulent, and the densities and flow-rates of the fluids are similar.

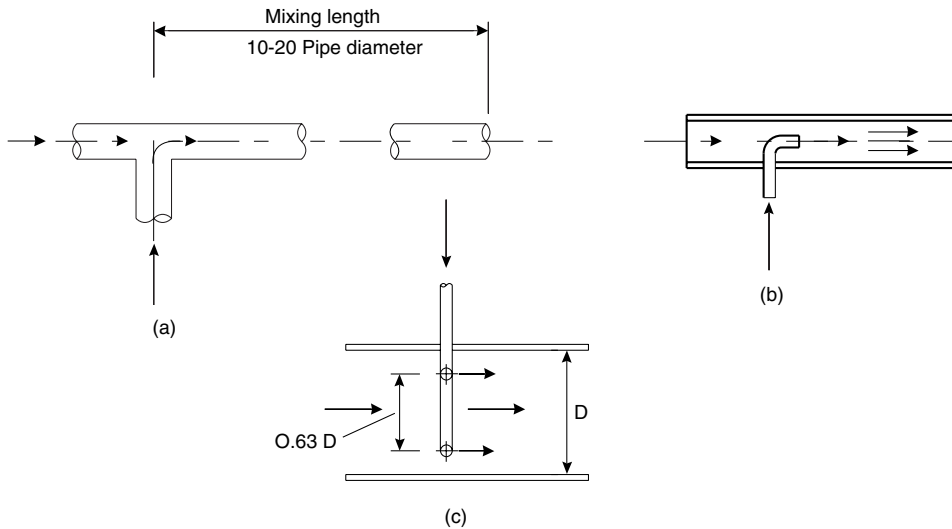


Figure 10.52. Inline mixers (a) Tee (b) Injection (c) Annular

With injection mixers (Figures 10.52b,c), in which the one fluid is introduced into the flowing stream of the other through a concentric pipe or an annular array of jets, mixing will take place by entrainment and turbulent diffusion. Such devices should be used where one flow is much lower than the other, and will give a satisfactory blend in about 80 pipe diameters. The inclusion of baffles or other flow restrictions will reduce the mixing length required.

The static inline mixer shown in Figure 10.53 is effective in both laminar and turbulent flow, and can be used to mix viscous mixtures. The division and rotation of the fluid at each element causes rapid radical mixing; see Rosenzweig (1977) and Baker (1991). The



Figure 10.53. Static mixer (Kenics Corporation)

dispersion and mixing of liquids in pipes is discussed by Zughi *et al.* (2003) and Lee and Brodkey (1964).

Centrifugal pumps are effective inline mixers for blending and dispersing liquids. Various proprietary motor-driven inline mixers are also used for special applications; see Perry *et al.* (1997).

### **Stirred tanks**

Mixing vessels fitted with some form of agitator are the most commonly used type of equipment for blending liquids and preparing solutions.

Liquid mixing in stirred tanks is covered in Volume 1, Chapter 7, and in several textbooks; Uhl and Gray (1967), Harnby *et al.* (1997) and Tatterson (1991), (1993).

A typical arrangement of the agitator and baffles in a stirred tank, and the flow pattern generated, is shown in Figure 10.54. Mixing occurs through the bulk flow of the liquid and, on a microscopic scale, by the motion of the turbulent eddies created by the agitator. Bulk flow is the predominant mixing mechanism required for the blending of miscible liquids and for solids suspension. Turbulent mixing is important in operations involving mass and heat transfer; which can be considered as shear controlled processes.

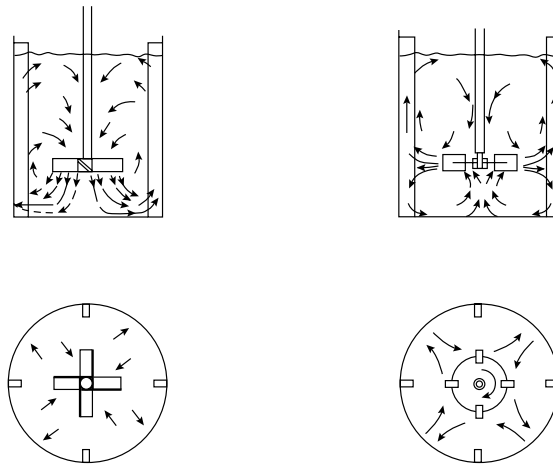
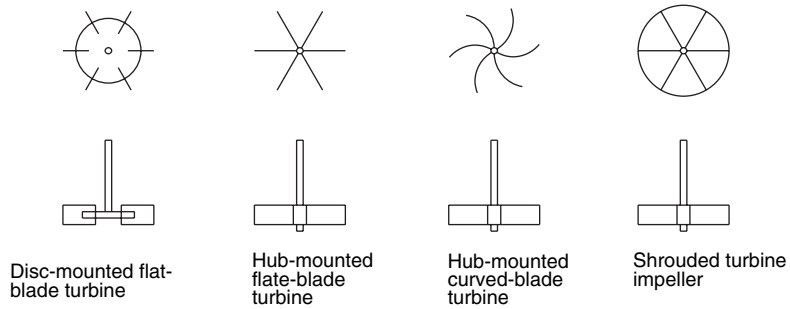


Figure 10.54. Agitator arrangements and flow patterns

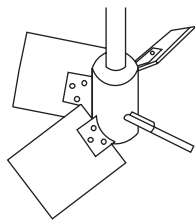
The most suitable agitator for a particular application will depend on the type of mixing required, the capacity of the vessel, and the fluid properties, mainly the viscosity.

The three basic types of impeller which are used at high Reynolds numbers (low viscosity) are shown in Figures 10.55*a, b, c*. They can be classified according to the predominant direction of flow leaving the impeller. The flat-bladed (Rushton) turbines are essentially radial-flow devices, suitable for processes controlled by turbulent mixing (shear controlled processes). The propeller and pitched-bladed turbines are essentially axial-flow devices, suitable for bulk fluid mixing.

Paddle, anchor and helical ribbon agitators (Figures 10.56*a, b, c*), and other special shapes, are used for more viscous fluids.



(a)

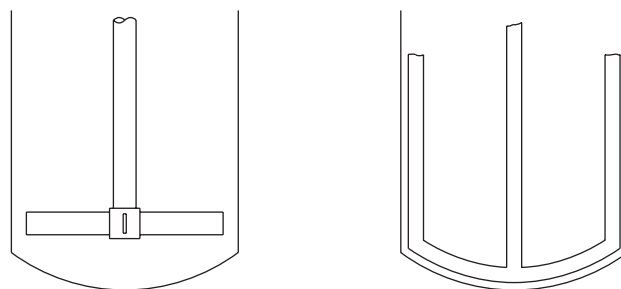


(b)



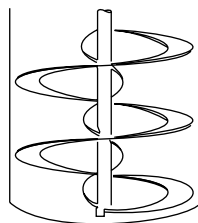
(c)

Figure 10.55. Basic impeller types (a) Turbine impeller (b) Pitched bladed turbine (c) Marine propeller



(a)

(b)



(c)

Figure 10.56. Low-speed agitators (a) Paddle (b) Anchor (c) Helical ribbon



The selection chart given in Figure 10.57, which has been adapted from a similar chart given by Penney (1970), can be used to make a preliminary selection of the agitator type, based on the liquid viscosity and tank volume.

For turbine agitators, impeller to tank diameter ratios of up to about 0.6 are used, with the depth of liquid equal to the tank diameter. Baffles are normally used, to improve the mixing and reduce problems from vortex formation. Anchor agitators are used with close clearance between the blades and vessel wall, anchor to tank diameter ratios of

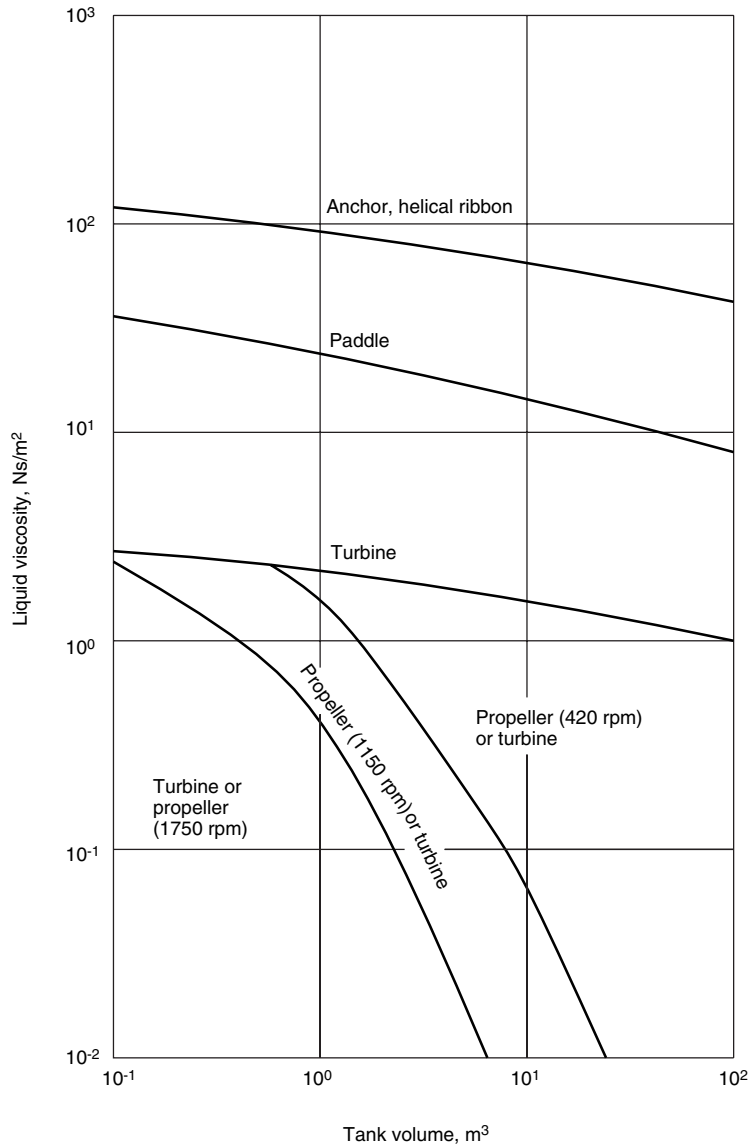


Figure 10.57. Agitator selection guide

0.95 or higher. The selection of agitators for dispersing gases in liquids is discussed by Hicks (1976).

### Agitator power consumption

The shaft power required to drive an agitator can be estimated using the following generalised dimensionless equation, the derivation of which is given in Volume 2, Chapter 13.

$$N_p = KRe^b Fr^c \quad (10.11)$$

where  $N_p$  = power number =  $\frac{P}{D^5 N^3 \rho}$ ,

$Re$  = Reynolds number =  $\frac{D^2 N \rho}{\mu}$ ,

$Fr$  = Froude number =  $\frac{DN^2}{g}$ ,

$P$  = shaft power, W,

$K$  = a constant, dependent on the agitator type, size, and the agitator-tank geometry,

$\rho$  = fluid density, kg/m<sup>3</sup>,

$\mu$  = fluid viscosity, Ns/m<sup>2</sup>,

$N$  = agitator speed, s<sup>-1</sup> (revolutions per second) (rps),

$D$  = agitator diameter, m,

$g$  = gravitational acceleration, 9.81 m/s<sup>2</sup>.

Values for the constant  $K$  and the indices  $b$  and  $c$  for various types of agitator, tank-agitator geometries, and dimensions, can be found in the literature; Rushton *et al.* (1950). A useful review of the published correlations for agitator power consumption and heat transfer in agitated vessels is given by Wilkinson and Edwards (1972); they include correlations for non-Newtonian fluids. Typical power curves for propeller and turbine agitators are given in Figures 10.58 and 10.59. In the laminar flow region the index “ $b$ ” = 1; and at high Reynolds number the power number is independent of the Froude number; index “ $c$ ” = 0.

An estimate of the power requirements for various applications can be obtained from Table 10.14.

Table 10.14. Power requirements—baffled agitated tanks

Agitation	Applications	Power, kW/m <sup>3</sup>
Mild	Blending, mixing	0.04–0.10
	Homogeneous reactions	0.01–0.03
Medium	Heat transfer	0.03–1.0
	Liquid-liquid mixing	1.0–1.5
Severe	Slurry suspension	1.5–2.0
	Gas absorption,	1.5–2.0
	Emulsions	1.5–2.0
Violent	Fine slurry suspension	>2.0

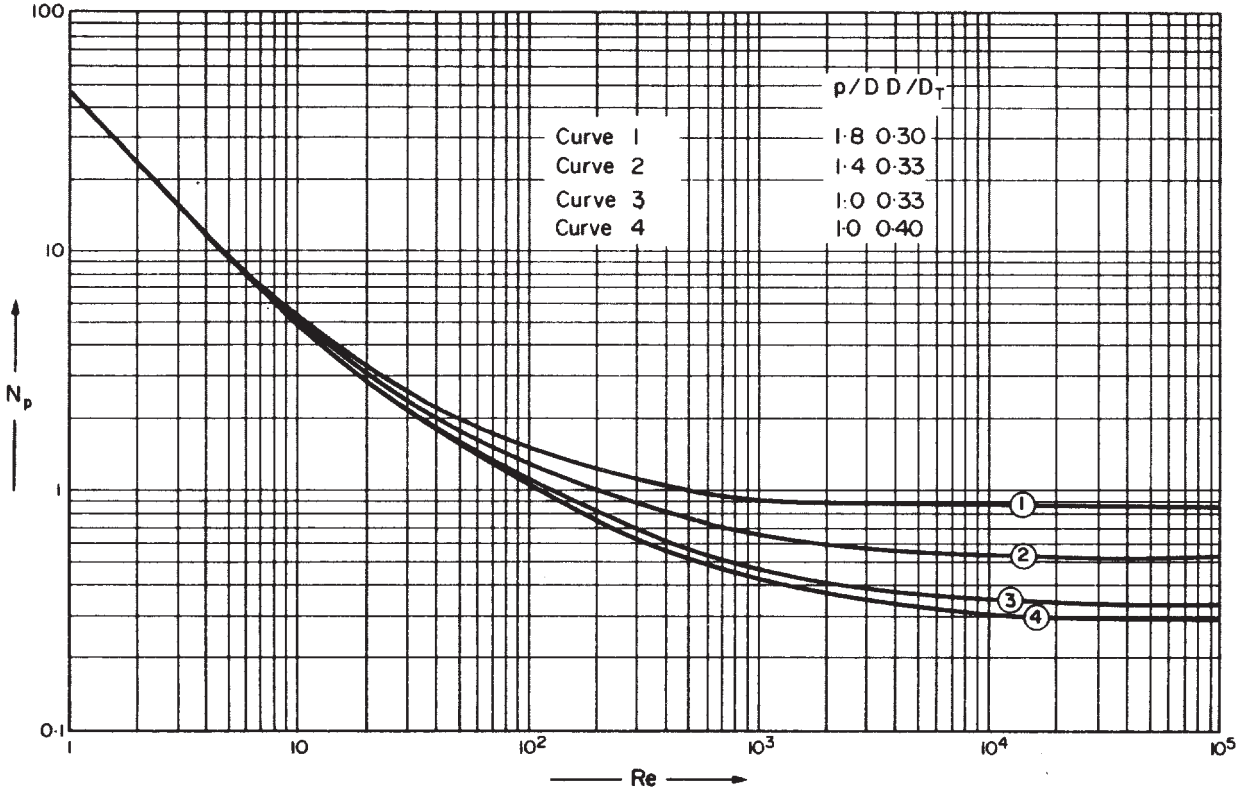


Figure 10.58. Power correlation for single three-bladed propellers baffled, (from Uhl and Gray (1967) with permission).  $p$  = blade pitch,  $D$  = impeller diameter,  $D_T$  = tank diameter

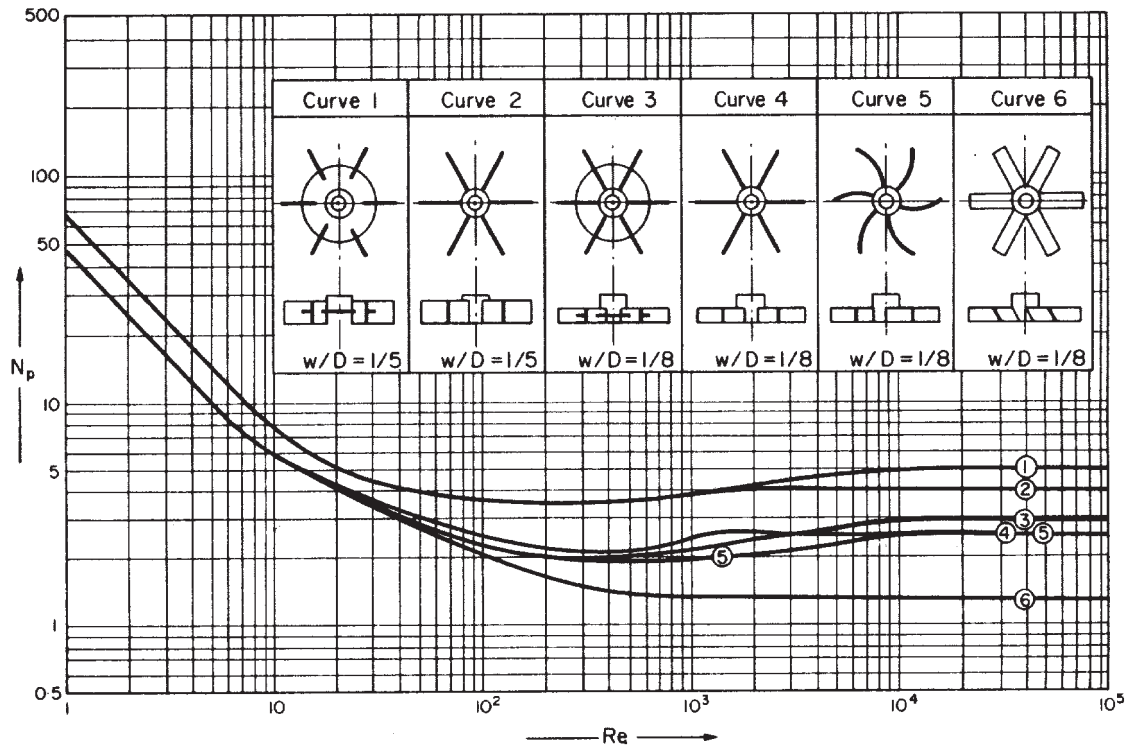


Figure 10.59. Power correlations for baffled turbine impellers, for tank with 4 baffles (From Uhl and Gray (1967) with permission).  $w$  = impeller width,  $D$  = impeller diameter

### ***Side-entering agitators***

Side-entering agitators are used for blending low viscosity liquids in large tanks, where it is impractical to use conventional agitators supported from the top of the tank; see Oldshue *et al.* (1956).

Where they are used with flammable liquids, particular care must be taken in the design and maintenance of the shaft seals, as any leakage may cause a fire.

For blending flammable liquids, the use of liquid jets should be considered as an “intrinsicly” safer option; see Fossett and Prosser (1949).

### **10.11.3. Solids and pastes**

A great variety of specialised equipment has been developed for mixing dry solids and pastes (wet solids). The principal types of equipment and their fields of application are given in Table 10.15. Descriptions of the equipment can be found in the literature; Perry *et al.* (1997), Reid (1979). Cone blenders are used for free-flowing solids. Ribbon blenders can be used for dry solids and for blending liquids with solids. Z-blade mixers and pan mixers are used for kneading heavy pastes and doughs. Most solid and paste mixers are designed for batch operation.

A selection chart for solids mixing equipment is given by Jones (1985).

Table 10.15. Solids and paste mixers

Type of equipment	Mixing action	Applications	Examples
Rotating: cone, double cone, drum	Tumbling action	Blending dry, free-flowing powders, granules, crystals	Pharmaceuticals, food, chemicals
Air blast fluidisation	Air blast lifts and mixes particles	Dry powders and granules	Milk powder; detergents, chemicals
Horizontal trough mixer, with ribbon blades, paddles or beaters	Rotating element produces contra-flow movement of materials	Dry and moist powders	Chemicals, food, pigments, tablet granulation
Z-blade mixers	Shearing and kneading by the specially shaped blades	Mixing heavy pastes, creams and doughs	Bakery industry, rubber doughs, plastic dispersions
Pan mixers	Vertical, rotating paddles, often with planetary motion	Mixing, whipping and kneading of materials ranging from low viscosity pastes to stiff doughs	Food, pharmaceuticals and chemicals, printing inks and ceramics
Cylinder mixers, single and double	Shearing and kneading action	Compounding of rubbers and plastics	Rubbers, plastics, and pigment dispersion

## **10.12. TRANSPORT AND STORAGE OF MATERIALS**

In this section the principal means used for the transport and storage of process materials: gases, liquids and solids are discussed briefly. Further details and full descriptions of the

equipment used can be found in various handbooks. Pumps and compressors are also discussed in Chapters 3 and 5 of this volume, and in Volume 1, Chapter 8.

### 10.12.1. Gases

The type of equipment best suited for the pumping of gases in pipelines depends on the flow-rate, the differential pressure required, and the operating pressure.

In general, fans are used where the pressure drop is small,  $<35 \text{ cm H}_2\text{O}$  (0.03 bar); axial flow compressors for high flow-rates and moderate differential pressures; centrifugal compressors for high flow-rates and, by staging, high differential pressures. Reciprocating compressors can be used over a wide range of pressures and capacities, but are normally only specified in preference to centrifugal compressors where high pressures are required at relatively low flow-rates.

Reciprocating, centrifugal and axial flow compressors are the principal types used in the chemical process industries, and the range of application of each type is shown in Figure 10.60 which has been adapted from a similar diagram by Dimoplon (1978). A more comprehensive selection guide is given in Table 10.16. Diagrammatic sketches of the compressors listed are given in Figure 10.61.

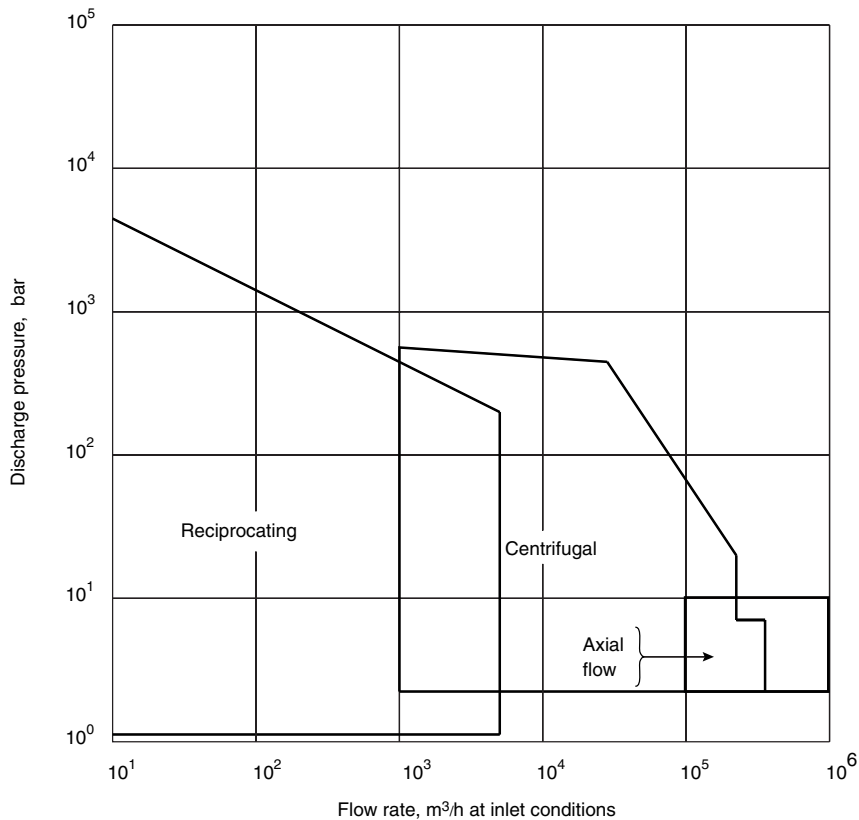


Figure 10.60. Compressor operating ranges

Table 10.16. Operating range of compressors and blowers (after Begg, 1966)

Type of compressor	Normal maximum speed (rpm)	Normal maximum capacity (m <sup>3</sup> /h)	Normal maximum pressure (differential) (bar)	
			Single stage	Multiple stage
<b>Displacement</b>				
1. Reciprocating	300	85,000	3.5	5000
2. Sliding vane	300	3400	3.5	8
3. Liquid ring	200	2550	0.7	1.7
4. Rootes	250	4250	0.35	1.7
5. Screw	10,000	12,750	3.5	17
<b>Dynamic</b>				
6. Centrifugal fan	1000	170,000		0.2
7. Turbo blower	3000	8500	0.35	1.7
8. Turbo compressor	10,000	136,000	3.5	100
9. Axial flow fan	1000	170,000	0.35	2.0
10. Axial flow blower	3000	170,000	3.5	10

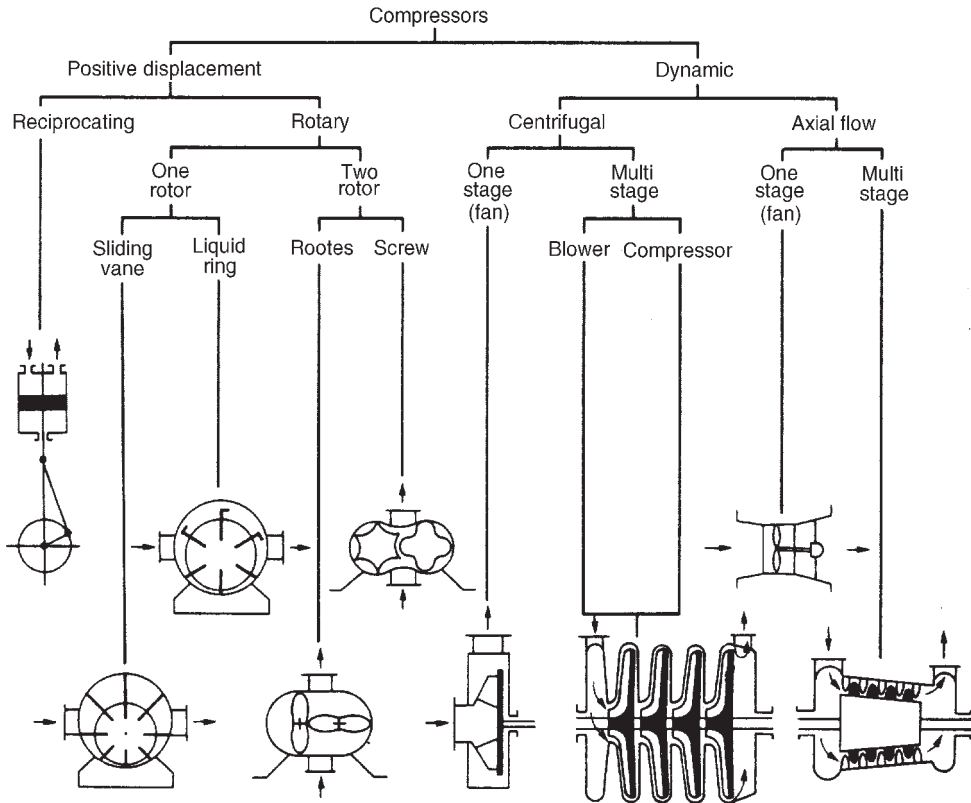


Figure 10.61. Type of compressor (Begg, 1966)

Several textbooks are available on compressor design, selection and operation: Bloch *et al.* (1982), Brown (1990) and Aungier (1999), (2003).

### ***Vacuum production***

The production of vacuum (sub-atmospheric pressure) is required for many chemical engineering processes; for example, vacuum distillation, drying and filtration. The type of vacuum pump needed will depend on the degree of vacuum required, the capacity of the system and the rate of air inleakage.

Reciprocating and rotary positive displacement pumps are commonly used where moderately low vacuum is required, about 10 mmHg (0.013 bar), at moderate to high flow rates; such as in vacuum filtration.

Steam-jet ejectors are versatile and economic vacuum pumps and are frequently used, particularly in vacuum distillation. They can handle high vapour flow rates and, by using several ejectors in series, can produce low pressures, down to about 0.1 mmHg (0.13 mbar).

The operating principle of steam-jet ejectors is explained in Volume 1, Chapter 8. Their specification, sizing and operation are covered in a comprehensive series of papers by Power (1964). Diffusion pumps are used where very low pressures are required (hard vacuum) for processes such as molecular distillation.

For a general reference on the design and application of vacuum system see Ryan and Roper (1986).

### ***Storage***

Gases are stored at low pressure in gas holders similar to those used for town gas, which are a familiar sight in any town. The liquid sealed type are most commonly used. These consist of a number of telescopic sections (lifts) which rise and fall as gas is added to or withdrawn from the holder. The dry sealed type is used where the gas must be kept dry. In this type the gas is contained by a piston moving in a large vertical cylindrical vessel. Water seal holders are intrinsically safer for use with flammable gases than the dry seal type; as any leakage through the piston seal may form an explosive mixture in the closed space between the piston and the vessel roof. Details of the construction of gas holders can be found in text books on Gas Engineering; Meade (1921), Smith (1945).

Gases are stored at high pressures where this is a process requirement and to reduce the storage volume. For some gases the volume can be further reduced by liquefying the gas by pressure or refrigeration. Cylindrical and spherical vessels (Horton spheres) are used. The design of pressure vessels is discussed in Chapter 13.

#### **10.12.2. Liquids**

The selection of pumps for liquids is discussed in Chapter 5. Descriptions of most of the types of pumps used in the chemical process industries are given in Volume 1, Chapter 8. Several textbooks and handbooks have also been published on this subject: Garay (1997), Karassik (2001) and Parmley (2000).

The principal types used and their operating pressures and capacity ranges are summarised in Table 10.17 and Figure 10.63. Centrifugal pumps will normally be the first



Table 10.17. Normal operating range of pumps

Type	Capacity range (m <sup>3</sup> /h)	Typical head (m of water)
Centrifugal	0.25–10 <sup>3</sup>	10–50 300 (multistage)
Reciprocating	0.5–500	50–200
Diaphragm	0.05–50	5–60
Rotary gear and similar	0.05–500	60–200
Rotary sliding vane or similar	0.25–500	7–70

choice for pumping process fluids, the other types only being used for special applications; such as the use of reciprocating and gear pumps for metering.

### **Pump shaft power**

The power required for pumping an incompressible fluid is given by:

$$\text{Power} = \frac{\Delta P Q_p}{\eta_p} \times 100 \quad (10.12)$$

where  $\Delta P$  = pressure differential across the pump, N/m<sup>2</sup>,

$Q_p$  = flow rate, m<sup>3</sup>/s,

$\eta_p$  = pump efficiency, per cent.

See also, Chapter 5, Section 5.4.3.

The efficiency of centrifugal pumps depends on their size. The values given in Figure 10.62 can be used to estimate the power and energy requirements for preliminary design purpose. The efficiency of reciprocating pumps is usually around 90 per cent.

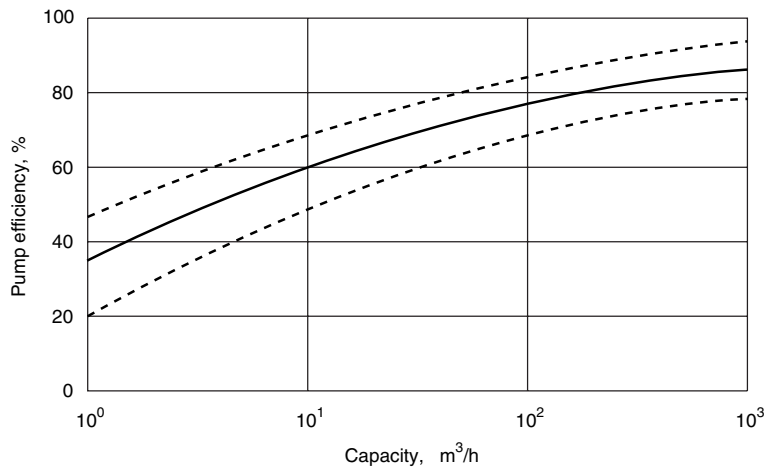


Figure 10.62. Efficiencies of centrifugal pumps

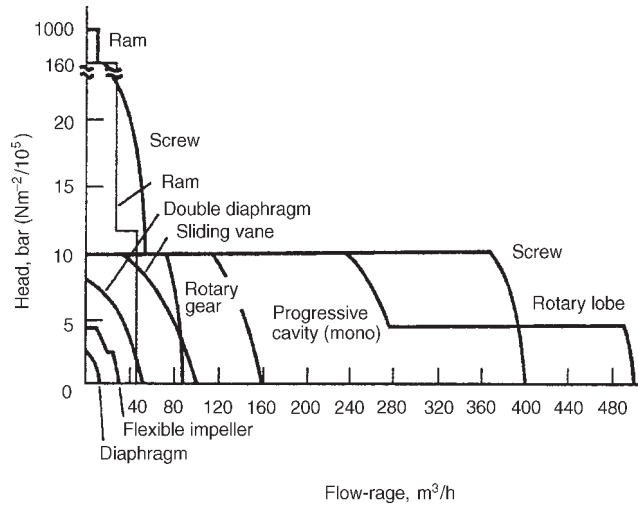


Figure 10.63. Selection of positive displacement pumps (adapted from Marshall (1985)). Descriptions of the types mentioned are given in Volume 1, Chapter 8

## Storage

Liquids are usually stored in bulk in vertical cylindrical steel tanks. Fixed and floating-roof tanks are used. In a floating-roof tank a movable piston floats on the surface of the liquid and is sealed to the tank walls. Floating-roof tanks are used to eliminate evaporation losses and, for flammable liquids, to obviate the need for inert gas blanketing to prevent an explosive mixture forming above the liquid, as would be the situation with a fixed-roof tank.

Horizontal cylindrical tanks and rectangular tanks are also used for storing liquids, usually for relatively small quantities.

The design of fixed roof, vertical tanks is discussed in Chapter 13, Section 13.16.

### 10.12.3. Solids

The movement and storage of solids is usually more expensive than the movement of liquids and gases, which can be easily pumped down a pipeline. The best equipment to use will depend on a number of factors:

1. The throughput.
2. Length of travel.
3. Change in elevation.
4. Nature of the solids: size, bulk density, angle of repose, abrasiveness, corrosiveness, wet or dry.

Belt conveyors are the most commonly used type of equipment for the continuous transport of solids. They can carry a wide range of materials economically over long and short distances; both horizontally or at an appreciable angle, depending on the angle of repose of the solids. A belt conveyor consists of an endless belt of a flexible material, supported on rollers (idlers), and passing over larger rollers at each end, one of which is

driven. The belt material is usually fabric-reinforced rubber or plastics; segmental metal belts are also used. Belts can be specified to withstand abrasive and corrosive materials; see BS 490.

Screw conveyors, also called worm conveyors, are used for materials that are free flowing. The basic principle of the screw conveyor has been known since the time of Archimedes. The modern conveyor consists of a helical screw rotating in a U-shaped trough. They can be used horizontally or, with some loss of capacity, at an incline to lift materials. Screw conveyors are less efficient than belt conveyors, due to the friction between the solids and the flights of the screw and the trough, but are cheaper and easier to maintain. They are used to convey solids over short distances, and when some elevation (lift) is required. They can also be used for delivering a metered flow of solids.

The most widely used equipment where a vertical lift is required is the bucket elevator. This consists of buckets fitted to an endless chain or belt, which passes over a driven roller or sprocket at the top end. Bucket elevators can handle a wide range of solids, from heavy lumps to fine powders, and are suitable for use with wet solids and slurries.

The mechanical conveying of solids is the subject of a book by Colijn (1985).

Pneumatic and hydraulic conveying, in which the solid particles are transported along a pipeline in suspension in a fluid, are discussed in Volume 1, Chapter 5, and in a book by Mills (2003); see also Mills *et al.* (2004).

### **Storage**

The simplest way to store solids is to pile them on the ground in the open air. This is satisfactory for the long-term storage of materials that do not deteriorate on exposure to the elements; for example, the seasonal stock piling of coal at collieries and power stations. For large stockpiles, permanent facilities are usually installed for distributing and reclaiming the material; travelling gantry cranes, grabs and drag scrapers feeding belt conveyors are used. For small, temporary, storages mechanical shovels and trunks can be used. Where the cost of recovery from the stockpile is large compared with the value of the stock held, storage in silos or bunkers should be considered.

Overhead bunkers, also called bins or hoppers, are normally used for the short-term storage of materials that must be readily available for the process. They are arranged so that the material can be withdrawn at a steady rate from the base of the bunker on to a suitable conveyor. Bunkers must be carefully designed to ensure the free flow of material within the bunker, to avoid packing and bridging. Jenike (1967) and Jenike and Johnson (1970), has studied the flow of solids in containers and developed design methods. All aspects of the design of bins and hoppers, including feeding and discharge systems, are covered in a book by Reisner (1971).

See also the British Material Handling Board's code of practice on the design of silos and bunkers, BMHB (1992).

The storage and transport of wet solids are covered by Heywood (1991).

## **10.13. REACTORS**

The reactor is the heart of a chemical process. It is the only place in the process where raw materials are converted into products, and reactor design is a vital step in the overall design of the process.

Numerous texts have been published on reactor design, and a selection is given in the bibliography at the end of this chapter. The volumes by Rase (1977), (1990) cover the practical aspects of reactor design and include case studies of industrial reactors. The design of electrochemical reactors is covered by Rousar *et al.* (1985) and Scott (1991).

The treatment of reactor design in this section will be restricted to a discussion of the selection of the appropriate reactor type for a particular process, and an outline of the steps to be followed in the design of a reactor.

The design of an industrial chemical reactor must satisfy the following requirements:

1. The chemical factors: the kinetics of the reaction. The design must provide sufficient residence time for the desired reaction to proceed to the required degree of conversion.
2. The mass transfer factors: with heterogeneous reactions the reaction rate may be controlled by the rates of diffusion of the reacting species; rather than the chemical kinetics.
3. The heat transfer factors: the removal, or addition, of the heat of reaction.
4. The safety factors: the confinement of hazardous reactants and products, and the control of the reaction and the process conditions.

The need to satisfy these interrelated, and often contradictory factors, makes reactor design a complex and difficult task. However, in many instances one of the factors will predominate and will determine the choice of reactor type and the design method.

### 10.13.1. Principal types of reactor

The following characteristics are normally used to classify reactor designs:

1. Mode of operation: batch or continuous.
2. Phases present: homogeneous or heterogeneous.
3. Reactor geometry: flow pattern and manner of contacting the phases
  - (i) stirred tank reactor;
  - (ii) tubular reactor;
  - (iii) packed bed, fixed and moving;
  - (iv) fluidised bed.

#### ***Batch or continuous processing***

In a batch process all the reagents are added at the commencement; the reaction proceeds, the compositions changing with time, and the reaction is stopped and the product withdrawn when the required conversion has been reached. Batch processes are suitable for small-scale production and for processes where a range of different products, or grades, is to be produced in the same equipment; for instance, pigments, dyestuffs and polymers.

In continuous processes the reactants are fed to the reactor and the products withdrawn continuously; the reactor operates under steady-state conditions. Continuous production will normally give lower production costs than batch production, but lacks the flexibility of batch production. Continuous reactors will usually be selected for large-scale production. Processes that do not fit the definition of batch or continuous are often referred to as

semi-continuous or semi-batch. In a semi-batch reactor some of the reactants may be added, or some of the products withdrawn, as the reaction proceeds. A semi-continuous process can be one which is interrupted periodically for some purpose; for instance, for the regeneration of catalyst.

### ***Homogeneous and heterogeneous reactions***

Homogeneous reactions are those in which the reactants, products, and any catalyst used form one continuous phase: gaseous or liquid.

Homogeneous gas phase reactors will always be operated continuously; whereas liquid phase reactors may be batch or continuous. Tubular (pipe-line) reactors are normally used for homogeneous gas-phase reactions; for example, in the thermal cracking of petroleum crude oil fractions to ethylene, and the thermal decomposition of dichloroethane to vinyl chloride. Both tubular and stirred tank reactors are used for homogeneous liquid-phase reactions.

In a heterogeneous reaction two or more phases exist, and the overriding problem in the reactor design is to promote mass transfer between the phases. The possible combination of phases are:

1. Liquid-liquid: immiscible liquid phases; reactions such as the nitration of toluene or benzene with mixed acids, and emulsion polymerisations.
2. Liquid-solid: with one, or more, liquid phases in contact with a solid. The solid may be a reactant or catalyst.
3. Liquid-solid-gas: where the solid is normally a catalyst; such as in the hydrogenation of amines, using a slurry of platinum on activated carbon as a catalyst.
4. Gas-solid: where the solid may take part in the reaction or act as a catalyst. The reduction of iron ores in blast furnaces and the combustion of solid fuels are examples where the solid is a reactant.
5. Gas-liquid: where the liquid may take part in the reaction or act as a catalyst.

### ***Reactor geometry (type)***

The reactors used for established processes are usually complex designs which have been developed (have evolved) over a period of years to suit the requirements of the process, and are unique designs. However, it is convenient to classify reactor designs into the following broad categories.

#### ***Stirred tank reactors***

Stirred tank (agitated) reactors consist of a tank fitted with a mechanical agitator and a cooling jacket or coils. They are operated as batch reactors or continuously. Several reactors may be used in series.

The stirred tank reactor can be considered the basic chemical reactor; modelling on a large scale the conventional laboratory flask. Tank sizes range from a few litres to several thousand litres. They are used for homogeneous and heterogeneous liquid-liquid and liquid-gas reactions; and for reactions that involve finely suspended solids, which are held in suspension by the agitation. As the degree of agitation is under the designer's control, stirred tank reactors are particularly suitable for reactions where good mass transfer or heat transfer is required.

When operated as a continuous process the composition in the reactor is constant and the same as the product stream, and, except for very rapid reactions, this will limit the conversion that can be obtained in one stage.

The power requirements for agitation will depend on the degree of agitation required and will range from about  $0.2 \text{ kW/m}^3$  for moderate mixing to  $2 \text{ kW/m}^3$  for intense mixing.

### ***Tubular reactor***

Tubular reactors are generally used for gaseous reactions, but are also suitable for some liquid-phase reactions.

If high heat-transfer rates are required, small-diameter tubes are used to increase the surface area to volume ratio. Several tubes may be arranged in parallel, connected to a manifold or fitted into a tube sheet in a similar arrangement to a shell and tube heat exchanger. For high-temperature reactions the tubes may be arranged in a furnace.

The pressure-drop and heat-transfer coefficients in empty tube reactors can be calculated using the methods for flow in pipes given in Volume 1.

### ***Packed bed reactors***

There are two basic types of packed-bed reactor: those in which the solid is a reactant, and those in which the solid is a catalyst. Many examples of the first type can be found in the extractive metallurgical industries.

In the chemical process industries the designer will normally be concerned with the second type: catalytic reactors. Industrial packed-bed catalytic reactors range in size from small tubes, a few centimetres diameter, to large diameter packed beds. Packed-bed reactors are used for gas and gas-liquid reactions. Heat-transfer rates in large diameter packed beds are poor and where high heat-transfer rates are required fluidised beds should be considered.

### ***Fluidised bed reactors***

The essential features of a fluidised bed reactor is that the solids are held in suspension by the upward flow of the reacting fluid; this promotes high mass and heat-transfer rates and good mixing. Heat-transfer coefficients in the order of  $200 \text{ W/m}^2\text{°C}$  to jackets and internal coils are typically obtained. The solids may be a catalyst; a reactant in fluidised combustion processes; or an inert powder, added to promote heat transfer.

Though the principal advantage of a fluidised bed over a fixed bed is the higher heat-transfer rate, fluidised beds are also useful where it is necessary to transport large quantities of solids as part of the reaction processes, such as where catalysts are transferred to another vessel for regeneration.

Fluidisation can only be used with relatively small sized particles,  $<300 \mu\text{m}$  with gases.

A great deal of research and development work has been done on fluidised bed reactors in recent years, but the design and scale up of large diameter reactors is still an uncertain process and design methods are largely empirical.

The principles of fluidisation processes are covered in Volume 2, Chapter 6. The design of fluidised bed reactors is discussed by Rase (1977).

### 10.13.2. Design procedure

A general procedure for reactor design is outlined below:

1. Collect together all the kinetic and thermodynamic data on the desired reaction and the side reactions. It is unlikely that much useful information will be gleaned from a literature search, as little is published in the open literature on commercially attractive processes. The kinetic data required for reactor design will normally be obtained from laboratory and pilot plant studies. Values will be needed for the rate of reaction over a range of operating conditions: pressure, temperature, flow-rate and catalyst concentration. The design of experimental reactors and scale-up is discussed by Rase (1977).
2. Collect the physical property data required for the design; either from the literature, by estimation or, if necessary, by laboratory measurements.
3. Identify the predominant rate-controlling mechanism: kinetic, mass or heat transfer. Choose a suitable reactor type, based on experience with similar reactions, or from the laboratory and pilot plant work.
4. Make an initial selection of the reactor conditions to give the desired conversion and yield.
5. Size the reactor and estimate its performance.  
Exact analytical solutions of the design relationships are rarely possible; semi-empirical methods based on the analysis of idealised reactors will normally have to be used.
6. Select suitable materials of construction.
7. Make a preliminary mechanical design for the reactor: the vessel design, heat-transfer surfaces, internals and general arrangement.
8. Cost the proposed design, capital and operating, and repeat steps 4 to 8, as necessary, to optimise the design.

In choosing the reactor conditions, particularly the conversion, and optimising the design, the interaction of the reactor design with the other process operations must not be overlooked. The degree of conversion of raw materials in the reactor will determine the size, and cost, of any equipment needed to separate and recycle unreacted materials. In these circumstances the reactor and associated equipment must be optimised as a unit.

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## 10.15. NOMENCLATURE

		Dimensions in MLT
$A_i$	Area of interface	$L^2$
$A_s$	Surface area of cyclone	$L^2$
$A_v$	Area for vapour flow	$L^2$
$A_1$	Area of cyclone inlet duct	$L^2$
$b$	Index in equation 10.11	—
$c$	Index in equation 10.11	—
$D$	Agitator diameter	$L$
$D_c$	Cyclone diameter	$L$
$D_{c1}$	Diameter of standard cyclone	$L$
$D_{c2}$	Diameter of proposed cyclone design	$L$
$D_T$	Tank diameter	$L$
$D_v$	minimum vessel diameter for separator	$L$
$d$	Particle diameter	$L$
$d_s$	Diameter of solid particle removed in a centrifuge	$L$
$d_1$	Mean diameter of particles separated in cyclone under standard conditions	$L$
$d_2$	Mean diameter of particles separated in proposed cyclone design	$L$
$d_{50}$	Particle diameter for which cyclone is 50 per cent efficient	$L$
$f_c$	Friction factor for cyclones	—
$f_v$	fraction of cross-sectional area occupied by vapour.	—
$h_v$	height above liquid level	$L$
$K$	Constant in equation 10.11	—
$L$	Cyclone feed volumetric flow-rate	$L^3T^{-1}$
$L_c$	Continuous phase volumetric flow-rate	$L^3T^{-1}$
$L_v$	length of separator	$LT^{-1}$
$l$	Length of decanter vessel	$L$
$N$	Agitator speed	$T^{-1}$
$P$	Agitator shaft power	$ML^2T^{-3}$
$\Delta P$	Press differential (pressure drop)	$ML^{-1}T^{-2}$
$p$	Agitator blade pitch	$L$
$Q$	Volumetric flow-rate of liquid through a centrifuge	$L^3T^{-1}$
$Q_p$	Volumetric liquid flow through a pump	$L^3T^{-1}$
$Q_1$	Standard flow-rate in cyclone	$L^3T^{-1}$
$Q_2$	Proposed flow-rate in cyclone	$L^3T^{-1}$
$r$	Radius of decanter vessel	$L$
$r_e$	Radius of cyclone exit pipe	$L$
$r_t$	Radius of circle to which centre line of cyclone inlet duct is tangential	$L$
$u_c$	Velocity of continuous phase in a decanter	$LT^{-1}$
$u_d$	Settling (terminal) velocity of dispersed phase in a decanter	$LT^{-1}$
$u_g$	Terminal velocity of solid particles settling under gravity	$LT^{-1}$
$u_s$	velocity in a separator	$LT^{-1}$
$u_t$	settling velocity	$LT^{-1}$
$\hat{u}_v$	Maximum allowable vapour velocity in a separating vessel	$LT^{-1}$
$u_1$	Velocity in cyclone inlet duct	$LT^{-1}$
$u_2$	Velocity in cyclone exit duct	$LT^{-1}$
$V_v$	Gas, or vapour volumetric flow-rate	$L^3T^{-1}$
$w$	Width of interface in a decanter	$L$
$z_1$	Height to light liquid overflow from a decanter	$L$
$z_2$	Height to heavy liquid overflow from a decanter	$L$
$z_3$	Height to the interface in a decanter	$L$
$\eta$	Separating efficiency of a centrifuge	—
$\eta_p$	Pump efficiency	—
$\mu$	Liquid viscosity	$ML^{-1}T^{-1}$
$\mu_c$	Viscosity of continuous phase	$ML^{-1}T^{-1}$
$\mu_1$	Cyclone test fluid viscosity	$ML^{-1}T^{-1}$

$\mu_2$	Viscosity of fluid in proposed cyclone design	$\text{ML}^{-1}\text{T}^{-1}$
$\rho$	Liquid density	$\text{ML}^{-3}$
$\rho_f$	Gas density	$\text{ML}^{-3}$
$\rho_L$	Liquid density	$\text{ML}^{-3}$
$\rho_s$	Density of solid	$\text{ML}^{-3}$
$\rho_v$	Vapour density	$\text{ML}^{-3}$
$\rho_1$	Light liquid density in a decanter	$\text{ML}^{-3}$
$\rho_2$	Heavy liquid density in a decanter	$\text{ML}^{-3}$
$\Delta\rho$	Difference in density between solid and liquid	$\text{ML}^{-3}$
$\Delta\rho_1$	Density difference under standard conditions in standard cyclone	$\text{ML}^{-3}$
$\Delta\rho_2$	Density difference in proposed cyclone design	$\text{ML}^{-3}$
$\Sigma$	Sigma value for centrifuges, defined by equation 10.1	$\text{L}^2$
$\phi$	Factor in Figure 10.48	—
$\psi$	Parameter in Figure 10.47	—

## 10.16. PROBLEMS

**10.1.** The product from a crystalliser is to be separated from the liquor using a centrifuge. The concentration of the crystals is 6.5 per cent and the slurry feed rate to the centrifuge will be  $5.0 \text{ m}^3/\text{h}$ . The density of the liquor is  $995 \text{ kg/m}^3$  and that of the crystals  $1500 \text{ kg/m}^3$ . The viscosity of the liquor is  $0.7 \text{ mN m}^{-2}\text{s}$ . The cut-off crystal size required is  $5 \mu\text{m}$ .  
Select a suitable type of centrifuge to use for this duty.

**10.2.** Dissolved solids in the tar from the bottom of a distillation column are precipitated by quenching the hot tar in oil. The solids are then separated from the oil and burnt. The density of the solids is  $1100 \text{ kg/m}^3$ . The density of the liquid phase after addition of the tar is  $860 \text{ kg/m}^3$  and its viscosity, at the temperature of the mixture,  $1.7 \text{ mN m}^{-2}\text{s}$ . The solid content of the oil and tar mixture is 10 per cent and the flow-rate of the liquid phase leaving the separator will be  $1000 \text{ kg/h}$ . The cut-off particle size required is  $0.1 \text{ mm}$ .  
List the types of separator that could be considered for separating the solids from the liquid. Bearing mind the nature of the process, what type of separator would you recommend for this duty?

**10.3.** The solids from a dilute slurry are to be separated using hydrocyclones. The density of the solids is  $2900 \text{ kg/m}^3$ , and liquid is water. A recovery of 95 per cent of particles greater than  $100 \mu\text{m}$  is required. The minimum operating temperature will be  $10^\circ\text{C}$  and the maximum  $30^\circ\text{C}$ .

Design a hydrocyclone system to handle  $1200 \text{ l/m}$  of this slurry.

**10.4.** A fluidised bed is used in the production of aniline by the hydrogenation of nitrobenzene. Single-stage cyclones, followed by candle filters, are used to remove fines from the gases leaving the fluidised bed.

The reactor operates at a temperature  $270^\circ\text{C}$  and a pressure of  $2.5 \text{ bara}$ . The reactor diameter is  $10 \text{ m}$ . Hydrogen is used in large excess in the reaction, and for the purposes of this exercise the properties of the gas may be taken as those of hydrogen at the reactor conditions. The density of the catalyst particles is  $1800 \text{ kg/m}^3$ .

The estimated particle size distribution of the fines is:

Particle size, $\mu\text{m}$	50	40	30	20	10	5	2
Percentage by weight less than	100	70	40	20	10	5	2

A 70 per cent recovery of the solids is required in the cyclones.

For a gas flow rate of  $100,000 \text{ m}^3/\text{h}$ , at the reactor conditions, determine how many cyclones operating in parallel are need and design a suitable cyclone. Estimate the size distribution of the particles entering the filters.

- 10.5.** In a process for the production of acrylic fibres by the emulsion polymerisation of acrylonitrile, the unreacted monomer is recovered from water by distillation. Acrylonitrile forms an azeotrope with water and the overhead product from the column contain around 5 mol per cent water. The overheads are condensed and the recovered acrylonitrile separated from the water in a decanter. The decanter operating temperature will be  $20^\circ\text{C}$ .

Size a suitable decanter for a feed-rate of  $3000 \text{ kg/h}$ .

- 10.6.** In the production of aniline by the hydrogenation of nitrobenzene, the reactor products are separated from unreacted hydrogen in a condenser. The condensate, which is mainly water and aniline, together with a small amount of unreacted nitrobenzene and cyclo-hexylamine, is fed to a decanter to separate the water and aniline. The separation will not be complete, as aniline is slightly soluble in water, and water in aniline. A typical material balance for the decanter is given below:

Basis 100 kg feed

	feed	aqueous stream	organic stream
water	23.8	21.4	2.4
aniline	72.2	1.1	71.1
nitrobenzene	3.2	trace	3.2
cyclo-hexylamine	0.8	0.8	trace
total	100	23.3	76.7

Design a decanter for this duty, for a feed-rate of  $3500 \text{ kg/h}$ . Concentrate on the separation of the water and aniline. The densities of water–aniline solutions are given in Appendix G, problem C.8. The decanter will operate at a maximum temperature of  $30^\circ\text{C}$ .

- 10.7.** Water droplets are to be separated from air in a simple separation drum. The flow-rate of the air is  $1000 \text{ m}^3/\text{h}$ , at stp, and it contains 75 kg of water. The drum will operate at 1.1 bara pressure and  $20^\circ\text{C}$ .

Size a suitable liquid–vapour separator.

- 10.8.** The vapours from a chlorine vaporiser will contain some liquid droplets. The vaporiser consists of a vertical, cylindrical, vessel with a submerged bundle for heating. A vapour rate of  $2500 \text{ kg/h}$  is required and the vaporiser will operate at 6 bara.

Size the vessel to restrict the carryover of liquid droplets. The liquid hold-up time need not be considered, as the liquid level will be a function of the thermal design.

# *Separation Columns*

## *(Distillation, Absorption and Extraction)*

### 11.1. INTRODUCTION

This chapter covers the design of separating columns. Though the emphasis is on distillation processes, the basic construction features, and many of the design methods, also apply to other multistage processes; such as stripping, absorption and extraction.

Distillation is probably the most widely used separation process in the chemical and allied industries; its applications ranging from the rectification of alcohol, which has been practised since antiquity, to the fractionation of crude oil.

Only a brief review of the fundamental principles that underlie the design procedures will be given; a fuller discussion can be found in Volume 2, and in other text books; King (1980), Hengstebeck (1976), Kister (1992).

A good understanding of methods used for correlating vapour-liquid equilibrium data is essential to the understanding of distillation and other equilibrium-staged processes; this subject was covered in Chapter 8.

In recent years, most of the work done to develop reliable design methods for distillation equipment has been carried out by a commercial organisation, Fractionation Research Inc., an organisation set up with the resources to carry out experimental work on full-size columns. Since their work is of a proprietary nature, it is not published in the open literature and it has not been possible to refer to their methods in this book. Fractionation Research's design manuals will, however, be available to design engineers whose companies are subscribing members of the organisation.

#### ***Distillation column design***

The design of a distillation column can be divided into the following steps:

1. Specify the degree of separation required: set product specifications.
2. Select the operating conditions: batch or continuous; operating pressure.
3. Select the type of contacting device: plates or packing.
4. Determine the stage and reflux requirements: the number of equilibrium stages.
5. Size the column: diameter, number of real stages.
6. Design the column internals: plates, distributors, packing supports.
7. Mechanical design: vessel and internal fittings.

The principal step will be to determine the stage and reflux requirements. This is a relatively simple procedure when the feed is a binary mixture, but a complex

and difficult task when the feed contains more than two components (multicomponent systems).

## 11.2. CONTINUOUS DISTILLATION: PROCESS DESCRIPTION

The separation of liquid mixtures by distillation depends on differences in volatility between the components. The greater the relative volatilities, the easier the separation. The basic equipment required for continuous distillation is shown in Figure 11.1. Vapour flows up the column and liquid counter-currently down the column. The vapour and liquid are brought into contact on plates, or packing. Part of the condensate from the condenser is returned to the top of the column to provide liquid flow above the feed point (reflux), and part of the liquid from the base of the column is vaporised in the reboiler and returned to provide the vapour flow.

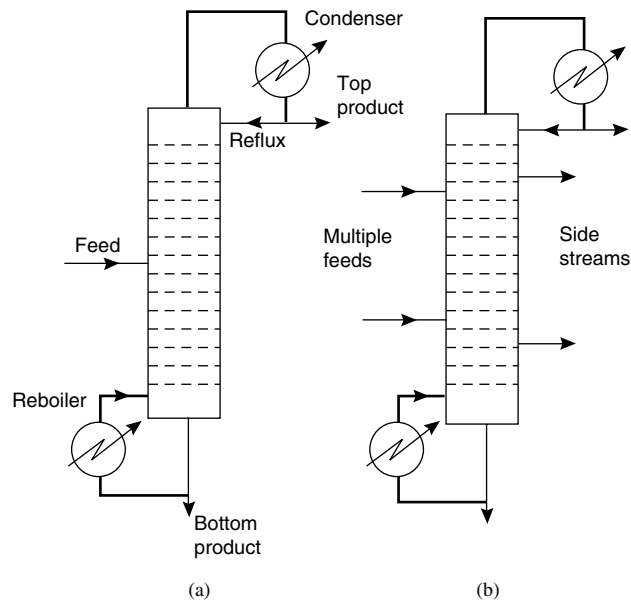


Figure 11.1. Distillation column (a) Basic column (b) Multiple feeds and side streams

In the section below the feed, the more volatile components are stripped from the liquid and this is known as the *stripping section*. Above the feed, the concentration of the more volatile components is increased and this is called the enrichment, or more commonly, the *rectifying section*. Figure 11.1a shows a column producing two product streams, referred to as *tops* and *bottoms*, from a single feed. Columns are occasionally used with more than one feed, and with side streams withdrawn at points up the column, Figure 11.1b. This does not alter the basic operation, but complicates the analysis of the process, to some extent.

If the process requirement is to strip a volatile component from a relatively non-volatile solvent, the rectifying section may be omitted, and the column would then be called a *stripping column*.

In some operations, where the top product is required as a vapour, only sufficient liquid is condensed to provide the reflux flow to the column, and the condenser is referred to as a partial condenser. When the liquid is totally condensed, the liquid returned to the column will have the same composition as the top product. In a partial condenser the reflux will be in equilibrium with the vapour leaving the condenser. Virtually pure top and bottom products can be obtained in a single column from a binary feed, but where the feed contains more than two components, only a single “pure” product can be produced, either from the top or bottom of the column. Several columns will be needed to separate a multicomponent feed into its constituent parts.

### 11.2.1. Reflux considerations

The reflux ratio,  $R$ , is normally defined as:

$$R = \frac{\text{flow returned as reflux}}{\text{flow of top product taken off}}$$

The number of stages required for a given separation will be dependent on the reflux ratio used.

In an operating column the effective reflux ratio will be increased by vapour condensed within the column due to heat leakage through the walls. With a well-lagged column the heat loss will be small and no allowance is normally made for this increased flow in design calculations. If a column is poorly insulated, changes in the internal reflux due to sudden changes in the external conditions, such as a sudden rain storm, can have a noticeable effect on the column operation and control.

#### **Total reflux**

Total reflux is the condition when all the condensate is returned to the column as reflux: no product is taken off and there is no feed.

At total reflux the number of stages required for a given separation is the minimum at which it is theoretically possible to achieve the separation. Though not a practical operating condition, it is a useful guide to the likely number of stages that will be needed.

Columns are often started up with no product take-off and operated at total reflux till steady conditions are attained. The testing of columns is also conveniently carried out at total reflux.

#### **Minimum reflux**

As the reflux ratio is reduced a *pinch point* will occur at which the separation can only be achieved with an infinite number of stages. This sets the minimum possible reflux ratio for the specified separation.



### ***Optimum reflux ratio***

Practical reflux ratios will lie somewhere between the minimum for the specified separation and total reflux. The designer must select a value at which the specified separation is achieved at minimum cost. Increasing the reflux reduces the number of stages required, and hence the capital cost, but increases the service requirements (steam and water) and the operating costs. The optimum reflux ratio will be that which gives the lowest annual operating cost. No hard and fast rules can be given for the selection of the design reflux ratio, but for many systems the optimum will lie between 1.2 to 1.5 times the minimum reflux ratio.

For new designs, where the ratio cannot be decided on from past experience, the effect of reflux ratio on the number of stages can be investigated using the short-cut design methods given in this chapter. This will usually indicate the best of value to use in more rigorous design methods.

At low reflux ratios the calculated number of stages will be very dependent on the accuracy of the vapour-liquid equilibrium data available. If the data are suspect a higher than normal ratio should be selected to give more confidence in the design.

### **11.2.2. Feed-point location**

The precise location of the feed point will affect the number of stages required for a specified separation and the subsequent operation of the column. As a general rule, the feed should enter the column at the point that gives the best match between the feed composition (vapour and liquid if two phases) and the vapour and liquid streams in the column. In practice, it is wise to provide two or three feed-point nozzles located round the predicted feed point to allow for uncertainties in the design calculations and data, and possible changes in the feed composition after start-up.

### **11.2.3. Selection of column pressure**

Except when distilling heat-sensitive materials, the main consideration when selecting the column operating-pressure will be to ensure that the dew point of the distillate is above that which can be easily obtained with the plant cooling water. The maximum, summer, temperature of cooling water is usually taken as 30°C. If this means that high pressures will be needed, the provision of refrigerated brine cooling should be considered. Vacuum operation is used to reduce the column temperatures for the distillation of heat-sensitive materials and where very high temperatures would otherwise be needed to distil relatively non-volatile materials.

When calculating the stage and reflux requirements it is usual to take the operating pressure as constant throughout the column. In vacuum columns, the column pressure drop will be a significant fraction of the total pressure and the change in pressure up the column should be allowed for when calculating the stage temperatures. This may require a trial and error calculation, as clearly the pressure drop cannot be estimated before an estimate of the number of stages is made.

## 11.3. CONTINUOUS DISTILLATION: BASIC PRINCIPLES

### 11.3.1. Stage equations

Material and energy balance equations can be written for any stage in a multistage process.

Figure 11.2 shows the material flows into and out of a typical stage  $n$  in a distillation column. The equations for this stage are set out below, for any component  $i$ .

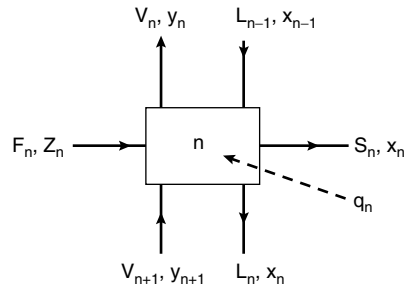


Figure 11.2. Stage flows

*material balance*

$$V_{n+1}y_{n+1} + L_{n-1}x_{n-1} + F_n z_n = V_n y_n + L_n x_n + S_n x_n \quad (11.1)$$

*energy balance*

$$V_{n+1}H_{n+1} + L_{n-1}h_{n-1} + Fh_f + q_n = V_n H_n + L_n h_n + S_n h_n \quad (11.2)$$

where  $V_n$  = vapour flow from the stage,

$V_{n+1}$  = vapour flow into the stage from the stage below,

$L_n$  = liquid flow from the stage,

$L_{n-1}$  = liquid flow into the stage from the stage above,

$F_n$  = any feed flow into the stage,

$S_n$  = any side stream from the stage,

$q_n$  = heat flow into, or removal from, the stage,

$n$  = any stage, numbered from the top of the column,

$z$  = mol fraction of component  $i$  in the feed stream (note, feed may be two-phase),

$x$  = mol fraction of component  $i$  in the liquid streams,

$y$  = mol fraction component  $i$  in the vapour streams,

$H$  = specific enthalpy vapour phase,

$h$  = specific enthalpy liquid phase,

$h_f$  = specific enthalpy feed (vapour + liquid).

All flows are the total stream flows (mols/unit time) and the specific enthalpies are also for the total stream (J/mol).

It is convenient to carry out the analysis in terms of “equilibrium stages”. In an equilibrium stage (theoretical plate) the liquid and vapour streams leaving the stage are taken to be in equilibrium, and their compositions are determined by the vapour-liquid equilibrium relationship for the system (see Chapter 8). In terms of equilibrium constants:

$$y_i = K_i x_i \quad (11.3)$$

The performance of real stages is related to an equilibrium stage by the concept of plate efficiencies for plate contactors, and “height of an equivalent theoretical plate” for packed columns.

In addition to the equations arising from the material and energy balances over a stage, and the equilibrium relationships, there will be a fourth relationship, the summation equation for the liquid and vapour compositions:

$$\sum x_{i,n} = \sum y_{i,n} = 1.0 \quad (11.4)$$

These four equations are the so-called MESH equations for the stage: Material balance, Equilibrium, Summation and Heat (energy) balance, equations. MESH equations can be written for each stage, and for the reboiler and condenser. The solution of this set of equations forms the basis of the rigorous methods that have been developed for the analysis for staged separation processes.

### 11.3.2. Dew points and bubble points

To estimate the stage, and the condenser and reboiler temperatures, procedures are required for calculating dew and bubble points. By definition, a saturated liquid is at its bubble point (any rise in temperature will cause a bubble of vapour to form), and a saturated vapour is at its dew point (any drop in temperature will cause a drop of liquid to form).

Dew points and bubble points can be calculated from a knowledge of the vapour-liquid equilibrium for the system. In terms of equilibrium constants, the bubble point is defined by the equation:

$$\text{bubble point: } \sum y_i = \sum K_i x_i = 1.0 \quad (11.5a)$$

$$\text{and dew point: } \sum x_i = \sum \frac{y_i}{K_i} = 1.0 \quad (11.5b)$$

For multicomponent mixtures the temperature that satisfies these equations, at a given system pressure, must be found by trial and error.

For binary systems the equations can be solved more readily because the component compositions are not independent; fixing one fixes the other.

$$y_a = 1 - y_b \quad (11.6a)$$

$$x_a = 1 - x_b \quad (11.6b)$$

Bubble- and dew-point calculations are illustrated in Example 11.9.

### 11.3.3. Equilibrium flash calculations

In an equilibrium flash process a feed stream is separated into liquid and vapour streams at equilibrium. The composition of the streams will depend on the quantity of the feed vaporised (flashed). The equations used for equilibrium flash calculations are developed below and a typical calculation is shown in Example 11.1.

Flash calculations are often needed to determine the condition of the feed to a distillation column and, occasionally, to determine the flow of vapour from the reboiler, or condenser if a partial condenser is used.

Single-stage flash distillation processes are used to make a coarse separation of the light components in a feed; often as a preliminary step before a multicomponent distillation column, as in the distillation of crude oil.

Figure 11.3 shows a typical equilibrium flash process. The equations describing this process are:

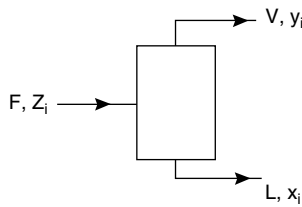


Figure 11.3. Flash distillation

Material balance, for any component,  $i$

$$Fz_i = Vy_i + Lx_i \quad (11.7)$$

Energy balance, total stream enthalpies:

$$Fh_f = VH + Lh \quad (11.8)$$

If the vapour-liquid equilibrium relationship is expressed in terms of equilibrium constants, equation 11.7 can be written in a more useful form:

$$\begin{aligned} Fz_i &= VK_i x_i + Lx_i \\ &= Lx_i \left[ \frac{V}{L} K_i + 1 \right] \end{aligned}$$

from which

$$L = \sum_i \frac{Fz_i}{\left[ \frac{VK_i}{L} + 1 \right]} \quad (11.9)$$

and, similarly,

$$V = \sum_i \frac{Fz_i}{\left[ \frac{L}{VK_i} + 1 \right]} \quad (11.10)$$

The groups incorporating the liquid and vapour flow-rates and the equilibrium constants have a general significance in separation process calculations.

The group  $L/VK_i$  is known as the absorption factor  $A_i$ , and is the ratio of the mols of any component in the liquid stream to the mols in the vapour stream.

The group  $VK_i/L$  is called the stripping factor  $S_i$ , and is the reciprocal of the absorption factor.

Efficient techniques for the solution of the trial and error calculations necessary in multicomponent flash calculations are given by several authors; Hengstebeck (1976) and King (1980).

### Example 11.1

A feed to a column has the composition given in the table below, and is at a pressure of 14 bar and a temperature of 60°C. Calculate the flow and composition of the liquid and vapour phases. Take the equilibrium data from the DePriester charts given in Chapter 8.

		kmol/h	$z_i$
Feed	ethane (C <sub>2</sub> )	20	0.25
	propane (C <sub>3</sub> )	20	0.25
	isobutane (iC <sub>4</sub> )	20	0.25
	n-pentane (nC <sub>5</sub> )	20	0.25

### Solution

For two phases to exist the flash temperature must lie between the bubble point and dew point of the mixture.

From equations 11.5a and 11.5b:

$$\sum K_i z_i > 1.0$$

$$\sum \frac{z_i}{K_i} > 1.0$$

Check feed condition

	$K_i$	$K_i z_i$	$z_i/K_i$
C <sub>2</sub>	3.8	0.95	0.07
C <sub>3</sub>	1.3	0.33	0.19
iC <sub>4</sub>	0.43	0.11	0.58
nC <sub>5</sub>	0.16	0.04	1.56
		$\Sigma$ 1.43	$\Sigma$ 2.40

therefore the feed is a two phase mixture.

## Flash calculation

	$K_i$	Try $L/V = 1.5$		Try $L/V = 3.0$	
		$A_i = L/VK_i$	$V_i = Fz_i/(1 + A_i)$	$A_i$	$V_i$
C <sub>2</sub>	3.8	0.395	14.34	0.789	11.17
C <sub>3</sub>	1.3	1.154	9.29	2.308	6.04
iC <sub>4</sub>	0.43	3.488	4.46	6.977	2.51
nC <sub>5</sub>	0.16	9.375	1.93	18.750	1.01
		$V_{\text{calc}} = 30.02$		$V_{\text{calc}} = 20.73$	
		$L/V = \frac{80 - 30.02}{30.02} = 1.67$		$L/V = 2.80$	

Hengstebeck's method is used to find the third trial value for  $L/V$ . The calculated values are plotted against the assumed values and the intercept with a line at  $45^\circ$  (calculated = assumed) gives the new trial value, 2.4.

	Try $L/V = 2.4$			
	$A_i$	$V_i$	$y_i = V_i/V$	$x_i = (Fz_i - V_i)/L$
C <sub>2</sub>	0.632	12.26	0.52	0.14
C <sub>3</sub>	1.846	7.03	0.30	0.23
iC <sub>4</sub>	5.581	3.04	0.13	0.30
nC <sub>5</sub>	15.00	1.25	0.05	0.33
		$V_{\text{cal}} = 23.58$	1.00	1.00
$L = 80 - 23.58 = 56.42$ kmol/h,				
$L/V$ calculated = $56.42/23.58 = 2.39$ close enough to the assumed value of 2.4.				

**Adiabatic flash**

In many flash processes the feed stream is at a higher pressure than the flash pressure and the heat for vaporisation is provided by the enthalpy of the feed. In this situation the flash temperature will not be known and must be found by trial and error. A temperature must be found at which both the material and energy balances are satisfied.

**11.4. DESIGN VARIABLES IN DISTILLATION**

It was shown in Chapter 1 that to carry out a design calculation the designer must specify values for a certain number of independent variables to define the problem completely, and that the ease of calculation will often depend on the judicious choice of these design variables.

In manual calculations the designer can use intuition in selecting the design variables and, as he proceeds with the calculation, can define other variables if it becomes clear that

the problem is not sufficiently defined. He can also start again with a new set of design variables if the calculations become tortuous. When specifying a problem for a computer method it is essential that the problem is completely and sufficiently defined.

In Chapter 1 it was shown that the number of independent variables for any problem is equal to the difference between the total number of variables and the number of linking equations and other relationships. Examples of the application of this formal procedure for determining the number of independent variables in separation process calculations are given by Gilliland and Reed (1942) and Kwauk (1956). For a multistage, multicomponent, column, there will be a set of material and enthalpy balance equations and equilibrium relationships for each stage (the MESH equations), and for the reboiler and condenser; for each component. If there are more than a few stages the task of counting the variables and equations becomes burdensome and mistakes are very likely to be made. A simpler, more practical, way to determine the number of independent variables is the "description rule" procedure given by Hanson *et al.* (1962). Their description rule states that to determine a separation process completely the number of independent variables which must be set (by the designer) will equal the number that are set in the construction of the column or that can be controlled by external means in its operation. The application of this rule requires the designer to visualise the column in operation and list the number of variables fixed by the column construction; those fixed by the process; and those that have to be controlled for the column to operate steadily and produce product within specification. The method is best illustrated by considering the operation of the simplest type of column: with one feed, no side streams, a total condenser, and a reboiler. The construction will fix the number of stages above and below the feed point (two variables). The feed composition and total enthalpy will be fixed by the processes upstream ( $1 + (\mathbf{n} - 1)$  variables, where  $\mathbf{n}$  is the number of components). The feed rate, column pressure and condenser and reboiler duties (cooling water and steam flows) will be controlled (four variables).

$$\text{Total number of variables fixed} = 2 + 1 + (\mathbf{n} - 1) + 4 = \underline{\underline{\mathbf{n} + 6}}$$

To design the column this number of variables must be specified completely to define the problem, but the same variables need not be selected.

Typically, in a design situation, the problem will be to determine the number of stages required at a specified reflux ratio and column pressure, for a given feed, and with the product compositions specified in terms of two key components and one product flow-rate. Counting up the number of variables specified it will be seen that the problem is completely defined:

Feed flow, composition, enthalpy	= $2 + (\mathbf{n} - 1)$
Reflux (sets $q_c$ )	= 1
Key component compositions, top and bottom	= 2
Product flow	= 1
Column pressure	= 1
	= $\mathbf{n} + 6$

*Note: specifying  $(\mathbf{n} - 1)$  component compositions completely defines the feed composition as the fractions add up to 1.*

In theory any  $(n + 6)$  independent variables could have been specified to define the problem, but it is clear that the use of the above variables will lead to a straightforward solution of the problem.

When replacing variables identified by the application of the description rule it is important to ensure that those selected are truly independent, and that the values assigned to them lie within the range of possible, practical, values.

The number of independent variables that have to be specified to define a problem will depend on the type of separation process being considered. Some examples of the application of the description rule to more complex columns are given by Hanson *et al.* (1962).

## 11.5. DESIGN METHODS FOR BINARY SYSTEMS

A good understanding of the basic equations developed for binary systems is essential to the understanding of distillation processes.

The distillation of binary mixtures is covered thoroughly in Volume 2, Chapter 11, and the discussion in this section is limited to a brief review of the most useful design methods. Though binary systems are usually considered separately, the design methods developed for multicomponent systems (Section 11.6) can obviously also be used for binary systems. With binary mixtures fixing the composition of one component fixes the composition of the other, and iterative procedures are not usually needed to determine the stage and reflux requirements; simple graphical methods are normally used.

### 11.5.1. Basic equations

Sorel (1899) first derived and applied the basic stage equations to the analysis of binary systems. Figure 11.4a shows the flows and compositions in the top part of a column. Taking the system boundary to include the stage  $n$  and the condenser, gives the following equations:

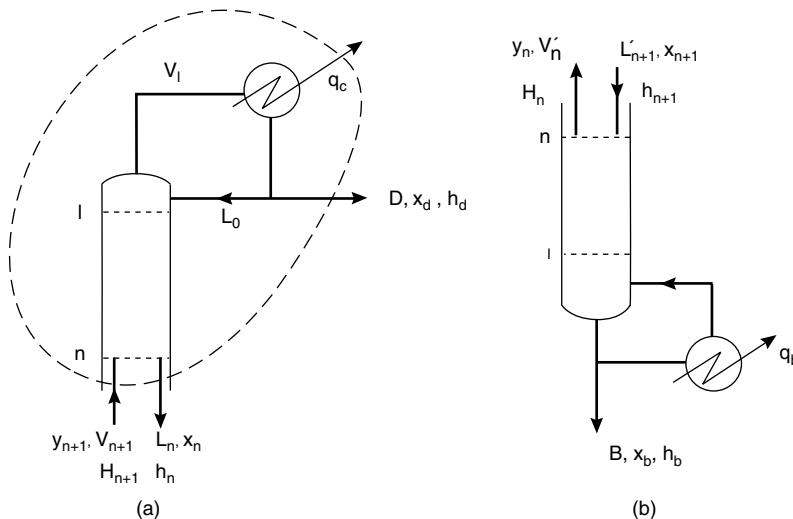


Figure 11.4. Column flows and compositions (a) Above feed (b) Below feed



*Material balance*

$$\text{total flows} \quad V_{n+1} = L_n + D \quad (11.11)$$

$$\text{for either component} \quad V_{n+1}y_{n+1} = L_nx_n + Dx_d \quad (11.12)$$

*Energy balance*

$$\text{total stream enthalpies} \quad V_{n+1}H_{n+1} = L_nh_n + Dh_d + q_c \quad (11.13)$$

where  $q_c$  is the heat removed in the condenser.

Combining equations 11.11 and 11.12 gives

$$y_{n+1} = \frac{L_n}{L_n + D}x_n + \frac{D}{L_n + D}x_d \quad (11.14)$$

Combining equations 11.11 and 11.13 gives

$$V_{n+1}H_{n+1} = (L_n + D)H_{n+1} = L_nh_n + Dh_d + q_c \quad (11.15)$$

Analogous equations can be written for the stripping section, Figure 11.6*b*.

$$x_{n+1} = \frac{V'_n}{V'_n + B}y_n + \frac{B}{V'_n + B}x_b \quad (11.16)$$

and

$$L'_{n+1}h_{n+1} = (V'_n + B)h_{n+1} = V'_nH_n + Bh_b - q_b \quad (11.17)$$

At constant pressure, the stage temperatures will be functions of the vapour and liquid compositions only (dew and bubble points) and the specific enthalpies will therefore also be functions of composition

$$H = f(y) \quad (11.18a)$$

$$h = f(x) \quad (11.18b)$$

***Lewis-Sorel method (equimolar overflow)***

For most distillation problems a simplifying assumption, first proposed by Lewis (1909), can be made that eliminates the need to solve the stage energy-balance equations. The molar liquid and vapour flow rates are taken as constant in the stripping and rectifying sections. This condition is referred to as equimolar overflow: the molar vapour and liquid flows from each stage are constant. This will only be true where the component molar latent heats of vaporisation are the same and, together with the specific heats, are constant over the range of temperature in the column; there is no significant heat of mixing; and the heat losses are negligible. These conditions are substantially true for practical systems when the components form near-ideal liquid mixtures.

Even when the latent heats are substantially different the error introduced by assuming equimolar overflow to calculate the number of stages is usually small, and acceptable.

With equimolar overflow equations 11.14 and 11.16 can be written without the subscripts to denote the stage number:

$$y_{n+1} = \frac{L}{L+D}x_n + \frac{D}{L+D}x_d \quad (11.19)$$

$$x_{n+1} = \frac{V'}{V'+B}y_n + \frac{B}{V'+B}x_b \quad (11.20)$$

where  $L$  = the constant liquid flow in the rectifying section = the reflux flow,  $L_0$ , and  $V'$  is the constant vapour flow in the stripping section.

Equations 11.19 and 11.20 can be written in an alternative form:

$$y_{n+1} = \frac{L}{V}x_n + \frac{D}{V}x_d \quad (11.21)$$

$$y_n = \frac{L'}{V'}x_{n+1} - \frac{B}{V'}x_b \quad (11.22)$$

where  $V$  is the constant vapour flow in the rectifying section =  $(L + D)$ ; and  $L'$  is the constant liquid flow in the stripping section =  $V' + B$ .

These equations are linear, with slopes  $L/V$  and  $L'/V'$ . They are referred to as *operating lines*, and give the relationship between the liquid and vapour compositions between stages. For an equilibrium stage, the compositions of the liquid and vapour streams leaving the stage are given by the equilibrium relationship.

### 11.5.2. McCabe-Thiele method

Equations 11.21 and 11.22 and the equilibrium relationship are conveniently solved by the graphical method developed by McCabe and Thiele (1925). The method is discussed fully in Volume 2. A simple procedure for the construction of the diagram is given below and illustrated in Example 11.2.

#### Procedure

Refer to Figure 11.5, all compositions are those of the more volatile component.

1. Plot the vapour-liquid equilibrium curve from data available at the column operating pressure. In terms of relative volatility:

$$y = \frac{\alpha x}{(1 + (\alpha - 1)x)} \quad (11.23)$$

where  $\alpha$  is the geometric average relative volatility of the lighter (more volatile) component with respect to the heavier component (less volatile).

It is usually more convenient, and less confusing, to use equal scales for the  $x$  and  $y$  axes.

2. Make a material balance over the column to determine the top and bottom compositions,  $x_d$  and  $x_b$ , from the data given.
3. The top and bottom operating lines intersect the diagonal at  $x_d$  and  $x_b$  respectively; mark these points on the diagram.
4. The point of intersection of the two operating lines is dependent on the phase condition of the feed. The line on which the intersection occurs is called the *q line* (see Volume 2). The *q line* is found as follows:

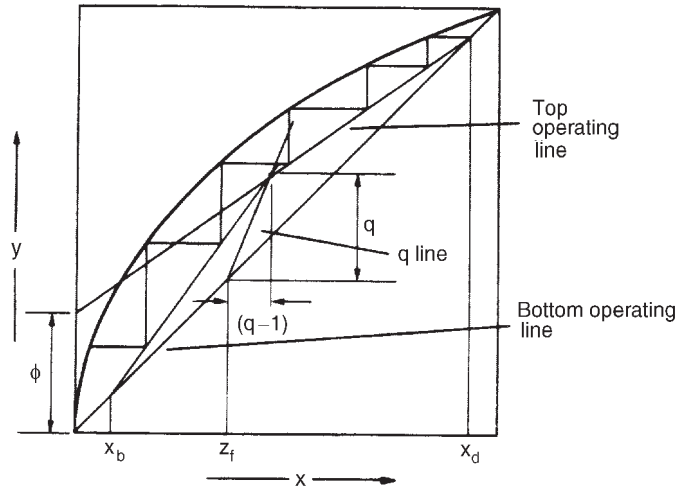


Figure 11.5. McCabe-Thiele diagram

- (i) calculate the value of the ratio  $q$  given by

$$q = \frac{\text{heat to vaporise 1 mol of feed}}{\text{molar latent heat of feed}}$$

- (ii) plot the  $q$  line, slope =  $q/(q - 1)$ , intersecting the diagonal at  $z_f$  (the feed composition).

5. Select the reflux ratio and determine the point where the top operating line extended cuts the  $y$  axis:

$$\phi = \frac{x_d}{1 + R} \quad (11.24)$$

6. Draw in the top operating line, from  $x_d$  on the diagonal to  $\phi$ .
7. Draw in the bottom operating line; from  $x_b$  on the diagonal to the point of intersection of the top operating line and the  $q$  line.
8. Starting at  $x_d$  or  $x_b$ , step off the number of stages.

*Note:* The feed point should be located on the stage closest to the intersection of the operating lines.

The reboiler, and a partial condenser if used, act as equilibrium stages. However, when designing a column there is little point in reducing the estimated number of stages to account for this; they can be considered additional factors of safety.

The efficiency of real contacting stages can be accounted for by reducing the height of the steps on the McCabe-Thiele diagram, see diagram Figure 11.6. Stage efficiencies are discussed in Section 11.10.

The McCabe-Thiele method can be used for the design of columns with side streams and multiple feeds. The liquid and vapour flows in the sections between the feed and take-off points are calculated and operating lines drawn for each section.

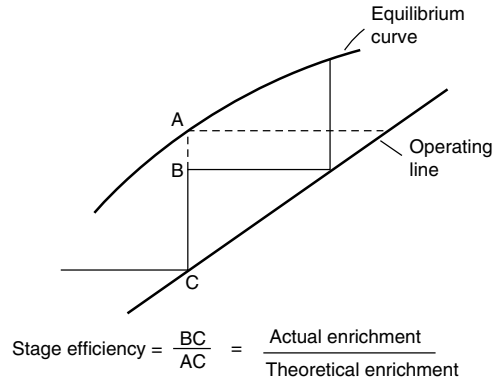


Figure 11.6. Stage efficiency

### Stage vapour and liquid flows not constant

The McCabe-Thiele method can be used when the condition of equimolar overflow cannot be assumed, but the operating lines will not then be straight. They can be drawn by making energy balances at a sufficient number of points to determine the approximate slope of the lines; see Hengstebeck (1976). Alternatively the more rigorous graphical method of Ponchon and Savarit derived in Volume 2 can be used. Nowadays, it should rarely be necessary to resort to complex graphical methods when the simple McCabe-Thiele diagram is not sufficiently accurate, as computer programs will normally be available for the rigorous solution of such problems.

### 11.5.3. Low product concentrations

When concentrations of the more volatile component of either product is very low the steps on the McCabe-Thiele diagram become very small and difficult to plot. This problem can be overcome by replotting the top or bottom sections to a larger scale, or on log-log paper. In a log plot the operating line will not be straight and must be drawn by plotting points calculated using equations 11.21 and 11.22. This technique is described by Alleva (1962) and is illustrated in Example 11.2.

If the operating and equilibrium lines are straight, and they usually can be taken as such when the concentrations are small, the number of stages required can be calculated using the equations given by Robinson and Gilliland (1950).

For the stripping section:

$$N_s^* = \frac{\log \left[ \frac{\left( \frac{K'}{s'} - 1 \right) \left( \frac{x_r'}{x_b} - 1 \right)}{\frac{1}{s'} (K' - 1)} + 1 \right]}{\log \left( \frac{K'}{s'} \right)} + 1 \quad (11.25)$$

where  $N_s^*$  = number of ideal stages required from  $x_b$  to some reference point  $x_r'$ ,  
 $x_b$  = mol fraction of the more volatile component in the bottom product,

- $x'_r$  = mol fraction of more volatile component at the reference point,  
 $s'$  = slope of the bottom operating line,  
 $K'$  = equilibrium constant for the more volatile component.

For the rectifying section:

$$N_r^* = \frac{\log \left[ \frac{(1-s) + x_r/x_d(s-K)}{1-K} \right]}{\log \left( \frac{s}{K} \right)} - 1 \quad (11.26)$$

- where  $N_r^*$  = number of stages required from some reference point  $x_r$  to the  $x_d$ ,  
 $x_d$  = mol fraction of the *least volatile* component in the top product,  
 $x_r$  = mol fraction of *least volatile* component at reference point,  
 $K$  = equilibrium constant for the *least volatile* component,  
 $s$  = slope of top operating line.

*Note:* at low concentrations  $K = \alpha$ .

The use of these equations is illustrated in Example 11.3.

### Example 11.2

Acetone is to be recovered from an aqueous waste stream by continuous distillation. The feed will contain 10 per cent w/w acetone. Acetone of at least 98 per cent purity is wanted, and the aqueous effluent must not contain more than 50 ppm acetone. The feed will be at 20°C. Estimate the number of ideal stages required.

### Solution

There is no point in operating this column at other than atmospheric pressure. The equilibrium data available for the acetone-water system were discussed in Chapter 8, Section 8.4.

The data of Kojima *et al.* will be used.

Mol fraction $x$ , liquid	0.00	0.05	0.10	0.15	0.20	0.25	0.30
Acetone $y$ , vapour	0.00	0.6381	0.7301	0.7716	0.7916	0.8034	0.8124
bubble point °C	100.0	74.80	68.53	65.26	63.59	62.60	61.87

$x$	0.35	0.40	0.45	0.50	0.55	0.60	0.65
$y$	0.8201	0.8269	0.8376	0.8387	0.8455	0.8532	0.8615
°C	61.26	60.75	60.35	59.95	59.54	59.12	58.71

$x$	0.70	0.75	0.80	0.85	0.90	0.95
$y$	0.8712	0.8817	0.8950	0.9118	0.9335	0.9627
°C	58.29	57.90	57.49	57.08	56.68	56.30

The equilibrium curve can be drawn with sufficient accuracy to determine the stages above the feed by plotting the concentrations at increments of 0.1. The diagram would normally be plotted at about twice the size of Figure 11.7.

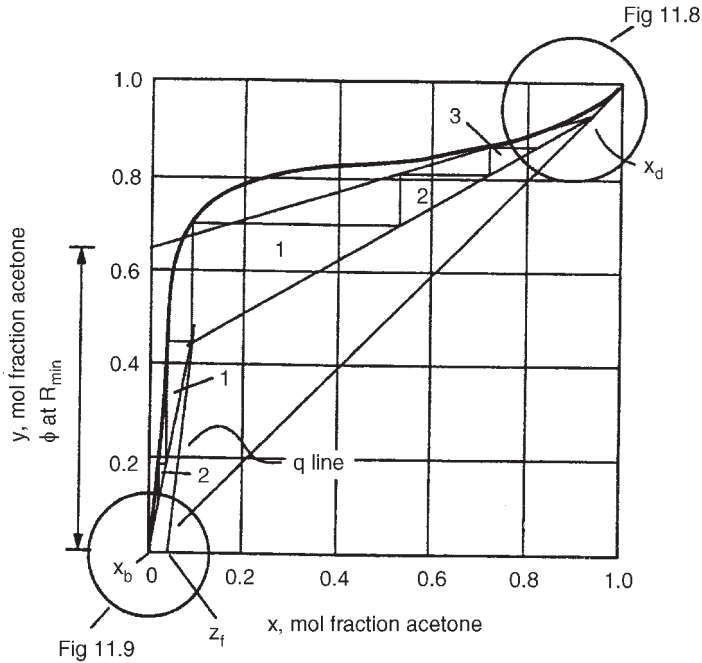


Figure 11.7. McCabe-Thiele plot, Example 11.2

Molecular weights, acetone 58, water 18

$$\text{Mol fractions acetone feed} = \frac{\frac{10}{58}}{\frac{10}{58} + \frac{90}{18}} = 0.033$$

$$\text{top product} = \frac{\frac{98}{58}}{\frac{98}{58} + \frac{2}{18}} = 0.94$$

$$\text{bottom product} = 50 \times 10^{-6} \times \frac{18}{58} = 15.5 \times 10^{-6}$$

### Feed condition (q-line)

Bubble point of feed (interpolated) = 83°C

Latent heats, water 41,360, acetone 28,410 J/mol

Mean specific heats, water 75.3, acetone 128 J/mol °C

Latent heat of feed =  $28,410 \times 0.033 + (1 - 0.033) 41,360 = 40,933$  J/mol

Specific heat of feed =  $(0.033 \times 128) + (1 - 0.033) 75.3 = 77.0$  J/mol °C

Heat to vaporise 1 mol of feed =  $(83 - 20) 77.0 + 40,933 = 45,784$  J

$$q = \frac{45,784}{40,933} = 1.12$$

$$\text{Slope of } q \text{ line} = \frac{1.12}{1.12 - 1} = 9.32$$

For this problem the condition of minimum reflux occurs where the top operating line just touches the equilibrium curve at the point where the  $q$  line cuts the curve.

From the Figure 11.7,

$$\phi \text{ for the operating line at minimum reflux} = 0.65$$

From equation 11.24,  $R_{\min} = 0.94/0.65 - 1 = 0.45$

Take  $R = R_{\min} \times 3$

As the flows above the feed point will be small, a high reflux ratio is justified; the condenser duty will be small.

$$\text{At } R = 3 \times 0.45 = 1.35, \quad \phi = \frac{0.94}{1 + 1.35} = 0.4$$

For this problem it is convenient to step the stages off starting at the intersection of the operating lines. This gives three stages above the feed up to  $y = 0.8$ . The top section is drawn to a larger scale, Figure 11.8, to determine the stages above  $y = 0.8$ : three to four stages required; total stages above the feed 7.

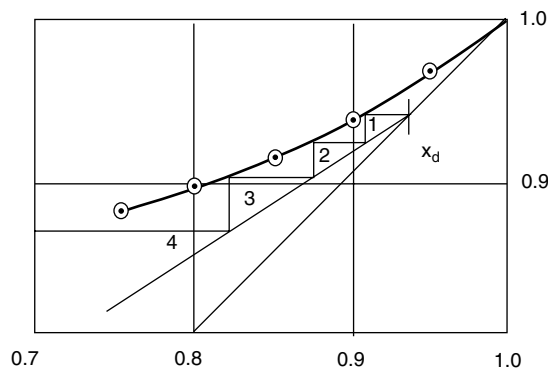


Figure 11.8. Top section enlarged

Below the feed, one stage is required down to  $x = 0.04$ . A log-log plot is used to determine the stages below this concentration. Data for log-log plot:

operating line slope, from Figure 11.7 =  $0.45/0.09 = 5.0$

operating line equation,  $y = 4.63(x - x_b) + x_b$

$$= 5.0x - 62.0 \times 10^{-6}$$

equilibrium line slope, from  $v-1-e$  data  $= 0.6381/0.05 = 12.8$

	$x = 4 \times 10^{-2}$	$10^{-3}$	$10^{-4}$	$4 \times 10^{-5}$	$2 \times 10^{-5}$
Equilibrium line $y =$	0.51	$1.3 \times 10^{-2}$	$1.3 \times 10^{-3}$	$5.1 \times 10^{-4}$	$2.6 \times 10^{-4}$
Operating line $y =$	0.20	$4.9 \times 10^{-3}$	$4.4 \times 10^{-4}$	$1.4 \times 10^{-4}$	$3.8 \times 10^{-5}$

From Figure 11.9, number of stages required for this section = 8

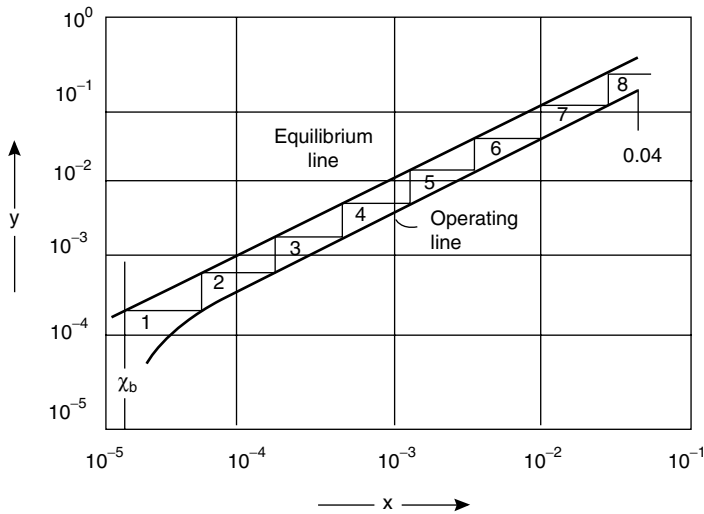


Figure 11.9. Log-log plot of McCabe-Thiele diagram

Total number of stages below feed = 9

Total stages =  $7 + 9 = \underline{\underline{16}}$

### Example 11.3

For the problem specified in Example 11.2, estimate the number of ideal stages required below an acetone concentration of 0.04 (more volatile component), using the Robinson-Gilliland equation.

### Solution

From the McCabe-Thiele diagram in Example 11.2:

slope of bottom operating line,  $s' = 5.0$

slope of equilibrium line,  $K' = 12.8$



$$x_b = 15.5 \times 10^{-6}$$

$$N_s^* = \frac{\log \left[ \frac{\left( \frac{12.8}{5.0} - 1 \right) \left( \frac{0.04}{15.5 \times 10^{-6}} - 1 \right)}{\left( \frac{1}{5.0} \right) (12.8 - 1)} + 1 \right]}{\log \left( \frac{12.8}{5.0} \right)} + 1 = 8.9, \underline{\underline{\text{say } 9}} \quad (11.25)$$

#### 11.5.4. The Smoker equations

Smoker (1938) derived an analytical equation that can be used to determine the number of stages when the relative volatility is constant. Though his method can be used for any problem for which the relative volatilities in the rectifying and stripping sections can be taken as constant, it is particularly useful for problems where the relative volatility is low; for example, in the separation of close boiling isomers. If the relative volatility is close to one, the number of stages required will be very large, and it will be impractical to draw a McCabe-Thiele diagram. The derivation of the equations are outlined below and illustrated in Example 11.4.

##### **Derivation of the equations:**

A straight operating line can be represented by the equation:

$$y = sx + c \quad (11.27)$$

and in terms of relative volatility the equilibrium values of  $y$  are given by:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (\text{equation 11.23})$$

Eliminating  $y$  from these equations gives a quadratic in  $x$ :

$$s(\alpha - 1)x^2 + [s + b(\alpha - 1) - \alpha]x + b = 0 \quad (11.28)$$

For any particular distillation problem equation 11.28 will have only one real root  $k$  between 0 and 1

$$s(\alpha - 1)k^2 + [s + b(\alpha - 1) - \alpha]k + b = 0 \quad (11.29)$$

$k$  is the value of the  $x$  ordinate at the point where the extended operating lines intersect the vapour-liquid equilibrium curve. Smoker shows that the number of stages required is given by the equation:

$$N = \log \left[ \frac{x_0^*(1 - \beta x_n^*)}{x_n^*(1 - \beta x_0^*)} \right] / \log \left( \frac{\alpha}{sc^2} \right) \quad (11.30)$$

where

$$\beta = \frac{sc(\alpha - 1)}{\alpha - sc^2} \quad (11.31)$$

$N$  = number of stages required to effect the separation represented by the concentration change from

$$x_n^* \text{ to } x_0^*; x^* = (x - k) \text{ and } x_0^* > x_n^* \\ c = 1 + (\alpha - 1)k \quad (11.32)$$

$s$  = slope of the operating line between  $x_n^*$  and  $x_0^*$ ,  
 $\alpha$  = relative volatility, assumed constant over  $x_n^*$  to  $x_0^*$ .

For a column with a single feed and no side streams:

### Rectifying section

$$x_0^* = x_d - k \quad (11.33)$$

$$x_n^* = z_f - k \quad (11.34)$$

$$s = \frac{R}{R+1} \quad (11.35)$$

$$b = \frac{x_d}{R+1} \quad (11.36)$$

### Stripping section

$$x_0^* = z_f - k \quad (11.37)$$

$$x_n^* = x_b - k \quad (11.38)$$

$$s = \frac{Rz_f + x_d - (R+1)x_b}{(R+1)(z_f - x_b)} \quad (11.39)$$

$$b = \frac{(z_f - x_d)x_b}{(R+1)(z_f - x_b)} \quad (11.40)$$

If the feed stream is not at its bubble point,  $z_f$  is replaced by the value of  $x$  at the intersection of operating lines, given by

$$z_f^* = \frac{b + \frac{z_f}{q-1}}{\frac{q}{q-1} - s} \quad (11.41)$$

All compositions for the more volatile component.

### Example 11.4

A column is to be designed to separate a mixture of ethylbenzene and styrene. The feed will contain 0.5 mol fraction styrene, and a styrene purity of 99.5 per cent is required, with a recovery of 85 per cent. Estimate the number of equilibrium stages required at a reflux ratio of 8. Maximum column bottom pressure 0.20 bar.

### Solution

Ethylbenzene is the more volatile component.

$$\text{Antoine equations, ethylbenzene, } \ln P^\circ = 9.386 - \frac{3279.47}{T - 59.95}$$

$$\text{styrene } \ln P^\circ = 9.386 - \frac{3328.57}{T - 63.72}$$

$P$  bar,  $T$  Kelvin

Material balance, basis 100 kmol feed:

at 85 per cent recovery, styrene in bottoms =  $50 \times 0.85 = 42.5$  kmol

at 99.5 per cent purity, ethylbenzene in bottoms =  $\frac{42.5}{99.5} \times 0.5 = 0.21$  kmol

ethylbenzene in the tops =  $50 - 0.21 = 49.79$  kmol

styrene in tops =  $50 - 42.5 = 7.5$  kmol

mol fraction ethylbenzene in tops =  $\frac{49.79}{49.79 + 7.5} = 0.87$

$z_f = 0.5$ ,  $x_b = 0.005$ ,  $x_d = 0.87$

Column bottom temperature, from Antoine equation for styrene

$$\ln 0.2 = 9.386 - \frac{3328.57}{T - 63.72}$$

$$T = 366 \text{ K}, 93.3^\circ\text{C}$$

At  $93.3^\circ\text{C}$ , vapour pressure of ethylbenzene

$$\ln P^\circ = 9.386 - \frac{3279.47}{366.4 - 59.95} = 0.27 \text{ bar}$$

$$\text{Relative volatility} = \frac{P^\circ \text{ ethylbenzene}}{P^\circ \text{ styrene}} = \frac{0.27}{0.20} = 1.35$$

The relative volatility will change as the compositions and (particularly for a vacuum column) the pressure changes up the column. The column pressures cannot be estimated until the number of stages is known; so as a first trial the relative volatility will be taken as constant, at the value determined by the bottom pressure.

### **Rectifying section**

$$s = \frac{8}{8 + 1} = 0.89 \quad (11.35)$$

$$b = \frac{0.87}{8 + 1} = 0.097 \quad (11.36)$$

$$0.89(1.35 - 1)k^2 + [0.89 + 0.097(1.35 - 1) - 1.35]k + 0.097 = 0 \quad (11.29)$$

$$k = 0.290$$

$$x_0^* = 0.87 - 0.29 = 0.58 \quad (11.33)$$

$$x_n^* = 0.50 - 0.29 = 0.21 \quad (11.34)$$

$$c = 1 + (1.35 - 1)0.29 = 1.10 \quad (11.32)$$

$$\beta = \frac{0.89 \times 1.10(1.35 - 1)}{1.35 - 0.89 \times 1.1^2} = 1.255 \quad (11.31)$$

$$N = \log \left[ \frac{0.58(1 - 1.255 \times 0.21)}{0.21(1 - 1.255 \times 0.58)} \right] / \log \left( \frac{1.35}{0.89 \times 1.1^2} \right) \quad (11.30)$$

$$= \frac{\log 7.473}{\log 1.254} = 8.87, \text{ say } \underline{\underline{9}}$$

**Stripping section**, feed taken as at its bubble point

$$s = \frac{8 \times 0.5 + 0.87 - (8 + 1)0.005}{(8 + 1)(0.5 - 0.005)} = 1.084 \quad (11.39)$$

$$b = \frac{(0.5 - 0.87)0.005}{(8 + 1)(0.5 - 0.005)} = -4.15 \times 10^{-4} \text{ (essentially zero)} \quad (11.40)$$

$$1.084(1.35 - 1)k^2 + [1.084 - 4.15 \times 10^{-4}(1.35 - 1) - 1.35]k - 4.15 \times 10^{-4}$$

$$k = 0.702 \quad (11.29)$$

$$x_0^* = 0.5 - 0.702 = -0.202 \quad (11.37)$$

$$x_n^* = 0.005 - 0.702 = -0.697 \quad (11.38)$$

$$c = 1 + (1.35 - 1)0.702 = 1.246 \quad (11.32)$$

$$\beta = \frac{1.084 \times 1.246(1.35 - 1)}{1.35 - 1.084 \times 1.246^2} = -1.42 \quad (11.31)$$

$$N = \log \left[ \frac{-0.202(1 - 0.697 \times 1.42)}{-0.697(1 - 0.202 \times 1.42)} \right] / \log \left( \frac{1.35}{1.084 \times 1.246^2} \right) \quad (11.30)$$

$$= \frac{\log[4.17 \times 10^{-3}]}{\log 0.8} = 24.6, \text{ say } \underline{\underline{25}}$$

## 11.6. MULTICOMPONENT DISTILLATION: GENERAL CONSIDERATIONS

The problem of determining the stage and reflux requirements for multicomponent distillations is much more complex than for binary mixtures. With a multicomponent mixture, fixing one component composition does not uniquely determine the other component compositions and the stage temperature. Also when the feed contains more than two components it is not possible to specify the complete composition of the top and bottom products independently. The separation between the top and bottom products is specified by setting limits on two “key” components, between which it is desired to make the separation.

The complexity of multicomponent distillation calculations can be appreciated by considering a typical problem. The normal procedure is to solve the MESH equations (Section 11.3.1) stage-by-stage, from the top and bottom of the column toward the feed point. For such a calculation to be exact, the compositions obtained from both the bottom-up and top-down calculations must mesh at the feed point and match the feed composition. But the calculated compositions will depend on the compositions assumed for the top and bottom products at the commencement of the calculations. Though it is possible to

match the key components, the other components will not match unless the designer was particularly fortunate in choosing the trial top and bottom compositions. For a completely rigorous solution the compositions must be adjusted and the calculations repeated until a satisfactory mesh at the feed point is obtained. Clearly, the greater the number of components, the more difficult the problem. As was shown in Section 11.3.2, trial-and-error calculations will be needed to determine the stage temperatures. For other than ideal mixtures, the calculations will be further complicated by the fact that the component volatilities will be functions of the unknown stage compositions. If more than a few stages are required, stage-by-stage calculations are complex and tedious; as illustrated in Example 11.9.

Before the advent of the modern digital computer, various “short-cut” methods were developed to simplify the task of designing multicomponent columns. A comprehensive summary of the methods used for hydrocarbon systems is given by Edmister (1947 to 1949) in a series of articles in the journal *The Petroleum Engineer*. Though computer programs will normally be available for the rigorous solution of the MESH equations, short-cut methods are still useful in the preliminary design work, and as an aid in defining problems for computer solution. Intelligent use of the short-cut methods can reduce the computer time and costs.

The short-cut methods available can be divided into two classes:

1. Simplification of the rigorous stage-by-stage procedures to enable the calculations to be done by hand, or graphically. Typical examples of this approach are the methods given by Smith and Brinkley (1960) and Hengstebeck (1976). These are described in Section 11.7 and Hengstebeck’s method is illustrated by a worked example.
2. Empirical methods, which are based on the performance of operating columns, or the results of rigorous designs. Typical examples of these methods are Gilliland’s correlation, which is given in Volume 2, Chapter 11, and the Erbar-Maddox correlation given in Section 11.7.3.

### 11.6.1. Key components

Before commencing the column design, the designer must select the two “key” components between which it is desired to make the separation. The light key will be the component that it is desired to keep out of the bottom product, and the heavy key the component to be kept out of the top product. Specifications will be set on the maximum concentrations of the keys in the top and bottom products. The keys are known as “adjacent keys” if they are “adjacent” in a listing of the components in order of volatility, and “split keys” if some other component lies between them in the order; they will usually be adjacent.

Which components are the key components will normally be clear, but sometimes, particularly if close boiling isomers are present, judgement must be used in their selection. If any uncertainty exists, trial calculations should be made using different components as the keys to determine the pair that requires the largest number of stages for separation (the worst case). The Fenske equation can be used for these calculations; see Section 11.7.3.

The “non-key” components that appear in both top and bottom products are known as “distributed” components; and those that are not present, to any significant extent, in one or other product, are known as “non-distributed” components.

### 11.6.2. Number and sequencing of columns

As was mentioned in Section 11.2, in multicomponent distillations it is not possible to obtain more than one pure component, one sharp separation, in a single column. If a multicomponent feed is to be split into two or more virtually pure products, several columns will be needed. Impure products can be taken off as side streams; and the removal of a side stream from a stage where a minor component is concentrated will reduce the concentration of that component in the main product.

For separation of  $N$  components, with one essentially pure component taken overhead, or from the bottom of each column,  $(N - 1)$  columns will be needed to obtain complete separation of all components. For example, to separate a mixture of benzene, toluene and xylene two columns are needed  $(3 - 1)$ . Benzene is taken overhead from the first column and the bottom product, essentially free of benzene, is fed to the second column. This column separates the toluene and xylene.

The order in which the components are separated will determine the capital and operating costs. Where there are several components the number of possible sequences can be very large; for example, with five components the number is 14, whereas with ten components it is near 5000. When designing systems that require the separation of several components, efficient procedures are needed to determine the optimum sequence of separation; see Doherty and Malone (2001), Smith (1995) and Kumar (1982).

Procedures for the sequencing of columns are also available in the commercial process simulator programs; for example, DISTIL in Hyprotech's suite of programs (see Chapter 4, Table 4.1).

In this section, it is only possible to give some general guide rules.

#### ***Heuristic rules for optimum sequencing***

1. Remove the components one at a time; as in the benzene-toluene-xylene example.
2. Remove any components that are present in large excess early in the sequence.
3. With difficult separations, involving close boiling components, postpone the most difficult separation to late in the sequence.

Difficult separations will require many stages, so to reduce cost, the column diameter should be made as small as possible. Column diameter is dependent on flow-rate; see Section 11.11. The further down the sequence the smaller will be the amount of material that the column has to handle.

#### ***Tall columns***

Where a large number of stages is required, it may be necessary to split a column into two separate columns to reduce the height of the column, even though the required separation could, theoretically, have been obtained in a single column. This may also be done in vacuum distillations, to reduce the column pressure drop and limit the bottom temperatures.

## **11.7. MULTICOMPONENT DISTILLATION: SHORT-CUT METHODS FOR STAGE AND REFLUX REQUIREMENTS**

Some of the more useful short-cut procedures which can be used to estimate stage and reflux requirements without the aid of computers are given in this section. Most of the

short-cut methods were developed for the design of separation columns for hydrocarbon systems in the petroleum and petrochemical systems industries, and caution must be exercised when applying them to other systems. They usually depend on the assumption of constant relative volatility, and should not be used for severely non-ideal systems.

Short-cut methods for non-ideal and azeotropic systems are given by Featherstone (1971) (1973).

### 11.7.1. Pseudo-binary systems

If the presence of the other components does not significantly affect the volatility of the key components, the keys can be treated as a pseudo-binary pair. The number of stages can then be calculated using a McCabe-Thiele diagram, or the other methods developed for binary systems. This simplification can often be made when the amount of the non-key components is small, or where the components form near-ideal mixtures.

Where the concentration of the non-keys is small, say less than 10 per cent, they can be lumped in with the key components. For higher concentrations the method proposed by Hengstebeck (1946) can be used to reduce the system to an equivalent binary system. Hengstebeck's method is outlined below and illustrated in Example 11.5. Hengstebeck's book (1976) should be consulted for the derivation of the method and further examples of its application.

#### *Hengstebeck's method*

For any component  $i$  the Lewis-Sorel material balance equations (Section 11.5) and equilibrium relationship can be written in terms of the individual component molar flow rates; in place of the component composition:

$$v_{n+1,i} = l_{n,i} + d_i \quad (11.42)$$

$$v_{n,i} = K_{n,i} \frac{V}{L} l_{n,i} \quad (11.43)$$

for the stripping section:

$$l'_{n+1,i} = v'_{n,i} + b_i \quad (11.44)$$

$$v'_{n,i} = K_{n,i} \frac{V'}{L'} l'_{n,i} \quad (11.45)$$

where  $l_{n,i}$  = the liquid flow rate of any component  $i$  from stage  $n$ ,

$v_{n,i}$  = the vapour flow rate of any component  $i$  from stage  $n$ ,

$d_i$  = the flow rate of component  $i$  in the tops,

$b_i$  = the flow rate of component  $i$  in the bottoms,

$K_{n,i}$  = the equilibrium constant for component  $i$  at stage  $n$ .

The superscript ' denotes the stripping section.

$V$  and  $L$  are the total flow-rates, assumed constant.

To reduce a multicomponent system to an equivalent binary it is necessary to estimate the flow-rate of the key components throughout the column. Hengstebeck makes use of the fact that in a typical distillation the flow-rates of each of the light non-key components approaches a constant, limiting, rate in the rectifying section; and the flows of each of the heavy non-key components approach limiting flow-rates in the stripping section. Putting

the flow-rates of the non-keys equal to these limiting rates in each section enables the combined flows of the key components to be estimated.

Rectifying section

$$L_e = L - \Sigma \underline{l}_i \quad (11.46)$$

$$V_e = V - \Sigma \underline{v}_i \quad (11.47)$$

Stripping section

$$L'_e = L' - \Sigma \underline{l}'_i \quad (11.48)$$

$$V'_e = V' - \Sigma \underline{v}'_i \quad (11.49)$$

where  $V_e$  and  $L_e$  are the estimated flow rates of the combined keys,

$\underline{l}_i$  and  $\underline{v}_i$  are the limiting liquid and vapour rates of components *lighter* than the keys in the rectifying section,

$\underline{l}'_i$  and  $\underline{v}'_i$  are the limiting liquid and vapour rates of components *heavier* than the keys in the stripping section.

The method used to estimate the limiting flow-rates is that proposed by Jenny (1939). The equations are:

$$\underline{l}_i = \frac{d_i}{\alpha_i - 1} \quad (11.50)$$

$$\underline{v}_i = l_i + d_i \quad (11.51)$$

$$\underline{v}'_i = \frac{\alpha_i b_i}{\alpha_{LK} - \alpha_i} \quad (11.52)$$

$$\underline{l}'_i = v'_i + b_i \quad (11.53)$$

where  $\alpha_i$  = relative volatility of component  $i$ , relative to the heavy key (HK),

$\alpha_{LK}$  = relative volatility of the light key (LK), relative to the heavy key.

Estimates of the flows of the combined keys enable operating lines to be drawn for the equivalent binary system. The equilibrium line is drawn by assuming a constant relative volatility for the light key:

$$y = \frac{\alpha_{LK} x}{1 + (\alpha_{LK} - 1)x} \quad (\text{equation 11.23})$$

where  $y$  and  $x$  refer to the vapour and liquid concentrations of the light key.

Hengstebeck shows how the method can be extended to deal with situations where the relative volatility cannot be taken as constant, and how to allow for variations in the liquid and vapour molar flow rates. He also gives a more rigorous graphical procedure based on the Lewis-Matheson method (see Section 11.8).

### Example 11.5

Estimate the number of ideal stages needed in the butane-pentane splitter defined by the compositions given in the table below. The column will operate at a pressure of 8.3 bar, with a reflux ratio of 2.5. The feed is at its boiling point.



*Note:* a similar problem has been solved by Lyster *et al.* (1959) using a rigorous computer method and it was found that ten stages were needed.

	Feed ( <i>f</i> )	Tops ( <i>d</i> )	Bottoms ( <i>b</i> )
Propane, C <sub>3</sub>	5	5	0
i-Butane, iC <sub>4</sub>	15	15	0
n-Butane, nC <sub>4</sub>	25	24	1
i-Pentane, iC <sub>5</sub>	20	1	19
n-Pentane, nC <sub>5</sub>	35	0	35
	100	45	55 kmol

### Solution

The top and bottom temperatures (dew points and bubble points) were calculated by the methods illustrated in Example 11.9. Relative volatilities are given by equation 8.30:

$$\alpha_i = \frac{K_i}{K_{HK}}$$

Equilibrium constants were taken from the Depriester charts (Chapter 8).

Relative volatilities

	Top	Bottom	Average
Temp. °C	65	120	
C <sub>3</sub>	5.5	4.5	5.0
iC <sub>4</sub>	2.7	2.5	2.6
(LK) nC <sub>4</sub>	2.1	2.0	2.0
(HK) iC <sub>5</sub>	1.0	1.0	1.0
nC <sub>5</sub>	0.84	0.85	0.85

Calculations of non-key flows

Equations 11.50, 11.51, 11.52, 11.53

	$\alpha_i$	$d_i$	$\underline{l}_i = d_i/(\alpha_i - 1)$	$\underline{v}_i = \underline{l}_i + d_i$
C <sub>3</sub>	5	5		6.3
iC <sub>4</sub>	2.6	15		24.4
		$\Sigma \underline{l}_i = 10.7$	$\Sigma \underline{v}_i = 30.7$	
	$\alpha_i$	$b_i$	$\underline{v}'_i = \alpha_i b_i/(\alpha_{LK} - \alpha_i)$	$\underline{l}'_i = \underline{v}'_i + b_i$
nC <sub>5</sub>	0.85	35	25.9	60.9
			$\Sigma \underline{v}'_i = 25.9$	$\Sigma \underline{l}'_i = 60.9$

Flows of combined keys

$$L_e = 2.5 \times 45 - 10.7 = 101.8 \quad (11.46)$$

$$V_e = (2.5 + 1)45 - 30.7 = 126.8 \quad (11.47)$$

$$V'_e = (2.5 + 1)45 - 25.9 = 131.6 \quad (11.49)$$

$$L'_e = (2.5 + 1)45 + 55 - 60.9 = 151.6 \quad (11.48)$$

Slope of top operating line

$$\frac{L_e}{V_e} = \frac{101.8}{126.8} = 0.8$$

Slope of bottom operating line

$$\frac{L'_e}{V'_e} = \frac{151.6}{131.6} = 1.15$$

$$x_b = \frac{\text{flow LK}}{\text{flow (LK + HK)}} = \frac{1}{19 + 1} = 0.05$$

$$x_d = \frac{24}{24 + 1} = 0.96$$

$$x_f = \frac{25}{25 + 20} = 0.56$$

$$y = \frac{2x}{1 + (2 - 1)x} = \frac{2x}{1 + x} \quad (11.23)$$

x	0	0.20	0.40	0.60	0.80	1.0
y	0	0.33	0.57	0.75	0.89	1.0

The McCabe-Thiele diagram is shown in Figure 11.10.

Twelve stages required; feed on seventh from base.

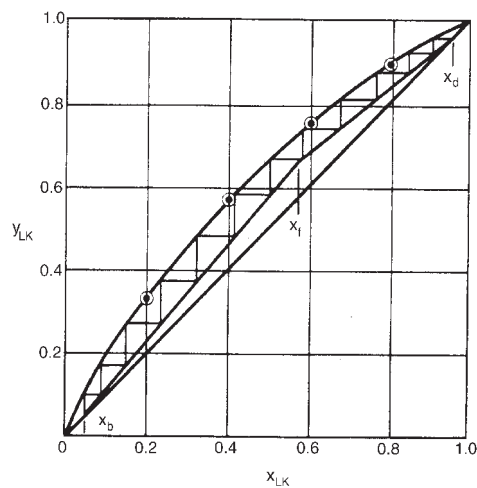


Figure 11.10. McCabe-Thiele diagram for Example 11.5

### 11.7.2. Smith-Brinkley method

Smith and Brinkley developed a method for determining the distribution of components in multicomponent separation processes. Their method is based on the solution of the finite-difference equations that can be written for multistage separation processes, and can be used for extraction and absorption processes, as well as distillation. Only the equations for distillation will be given here. The derivation of the equations is given by Smith and Brinkley (1960) and Smith (1963). For any component  $i$  (suffix  $i$  omitted in the equation for clarity)

$$\frac{b}{f} = \frac{(1 - S_r^{N_r - N_s}) + R(1 - S_r)}{(1 - S_r^{N_r - N_s}) + R(1 - S_r) + GS_r^{N_r - N_s}(1 - S_s^{N_s + 1})} \quad (11.54)$$

where  $b/f$  is the fractional split of the component between the feed and the bottoms, and:

$N_r$  = number of equilibrium stages above the feed,

$N_s$  = number of equilibrium stages below the feed,

$S_r$  = stripping factor, rectifying section =  $K_i V/L$ ,

$S_s$  = stripping factor, stripping section =  $K'_i V'/L'$ ,

$V$  and  $L$  are the total molar vapour and liquid flow rates, and the superscript ' denotes the stripping section.

$G$  depends on the condition of the feed.

If the feed is mainly liquid:

$$G_i = \frac{K'_i L}{K_i L'} \left[ \frac{1 - S_r}{1 - S_s} \right]_i \quad (11.55)$$

and the feed stage is added to the stripping section.

If the feed is mainly vapour:

$$G_i = \frac{L}{L'} \left[ \frac{1 - S_r}{1 - S_s} \right]_i \quad (11.56)$$

Equation 11.54 is for a column with a total condenser. If a partial condenser is used the number of stages in the rectifying section should be increased by one.

The procedure for using the Smith-Brinkley method is as follows:

1. Estimate the flow-rates  $L$ ,  $V$  and  $L'$ ,  $V'$  from the specified component separations and reflux ratio.
2. Estimate the top and bottom temperatures by calculating the dew and bubble points for assumed top and bottom compositions.
3. Estimate the feed point temperature.
4. Estimate the average component  $K$  values in the stripping and rectifying sections.
5. Calculate the values of  $S_{r,i}$  for the rectifying section and  $S_{s,i}$  for the stripping section.

6. Calculate the fractional split of each component, and hence the top and bottom compositions.
7. Compare the calculated with the assumed values and check the overall column material balance.
8. Repeat the calculation until a satisfactory material balance is obtained. The usual procedure is to adjust the feed temperature up and down till a satisfactory balance is obtained.

Examples of the application of the Smith-Brinkley method are given by Smith (1963).

This method is basically a rating method, suitable for determining the performance of an existing column, rather than a design method, as the number of stages must be known.

It can be used for design by estimating the number of stages by some other method and using equation 11.54 to determine the top and bottom compositions. The estimated stages can then be adjusted and the calculations repeated until the required specifications are achieved. However, the Geddes-Hengstebeck method for estimating the component splits, described in Section 11.7.4, is easier to use and satisfactory for preliminary design.

### 11.7.3. Empirical correlations

The two most frequently used empirical methods for estimating the stage requirements for multicomponent distillations are the correlations published by Gilliland (1940) and by Erbar and Maddox (1961). These relate the number of ideal stages required for a given separation, at a given reflux ratio, to the number at total reflux (minimum possible) and the minimum reflux ratio (infinite number of stages).

Gilliland's correlation is given in Volume 2, Chapter 11.

The Erbar-Maddox correlation is given in this section, as it is now generally considered to give more reliable predictions. Their correlation is shown in Figure 11.11; which gives the ratio of number of stages required to the number at total reflux, as a function of the reflux ratio, with the minimum reflux ratio as a parameter. To use Figure 11.11, estimates of the number of stages at total reflux and the minimum reflux ratio are needed.

#### ***Minimum number of stages (Fenske equation)***

The Fenske equation (Fenske, 1932) can be used to estimate the minimum stages required at total reflux. The derivation of this equation for a binary system is given in Volume 2, Chapter 11. The equation applies equally to multicomponent systems and can be written as:

$$\left[ \frac{x_i}{x_r} \right]_d = \alpha_i^{N_m} \left[ \frac{x_i}{x_r} \right]_b \quad (11.57)$$

where  $[x_i/x_r]$  = the ratio of the concentration of any component  $i$  to the concentration of a reference component  $r$ , and the suffixes  $d$  and  $b$  denote the distillate (tops) ( $d$ ) and the bottoms ( $b$ ),

$N_m$  = minimum number of stages at total reflux, including the reboiler,

$\alpha_i$  = average relative volatility of the component  $i$  with respect to the reference component.

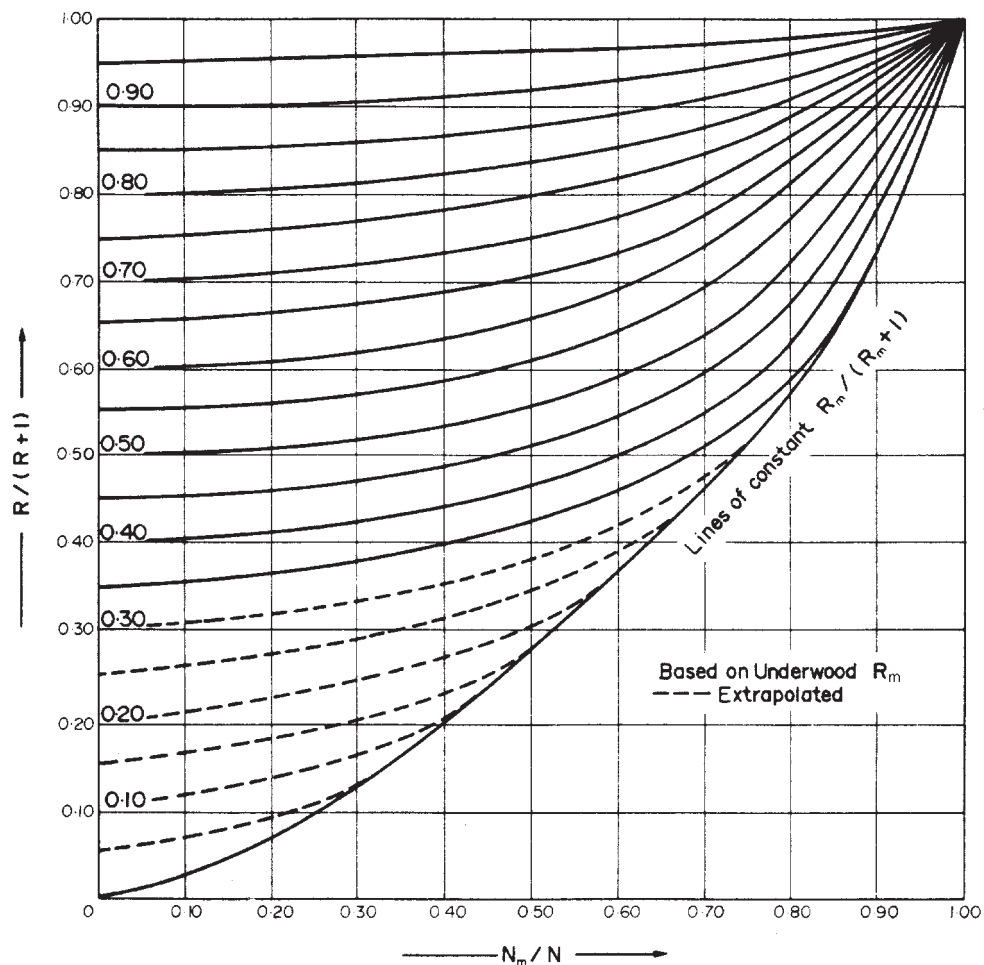


Figure 11.11. Erbar-Maddox correlation (Erbar and Maddox, 1961)

Normally the separation required will be specified in terms of the key components, and equation 11.57 can be rearranged to give an estimate of the number of stages.

$$N_m = \frac{\log \left[ \frac{x_{LK}}{x_{HK}} \right]_d \left[ \frac{x_{HK}}{x_{LK}} \right]_b}{\log \alpha_{LK}} \quad (11.58)$$

where  $\alpha_{LK}$  is the average relative volatility of the light key with respect to the heavy key, and  $x_{LK}$  and  $x_{HK}$  are the light and heavy key concentrations. The relative volatility is taken as the geometric mean of the values at the column top and bottom temperatures. To calculate these temperatures initial estimates of the compositions must be made, so the calculation of the minimum number of stages by the Fenske equation is a trial-and-error procedure. The procedure is illustrated in Example 11.7. If there is a wide

difference between the relative volatilities at the top and bottom of the column the use of the average value in the Fenske equation will underestimate the number of stages. In these circumstances, a better estimate can be made by calculating the number of stages in the rectifying and stripping sections separately; taking the feed concentration as the base concentration for the rectifying section and as the top concentration for the stripping section, and estimating the average relative volatilities separately for each section. This procedure will also give an estimate of the feed point location.

Winn (1958) has derived an equation for estimating the number of stages at total reflux, which is similar to the Fenske equation, but which can be used when the relative volatility cannot be taken as constant.

If the number of stages is known, equation 11.57 can be used to estimate the split of components between the top and bottom of the column at total reflux. It can be written in a more convenient form for calculating the split of components:

$$\frac{d_i}{b_i} = \alpha_i^{N_m} \left[ \frac{d_r}{b_r} \right] \quad (11.59)$$

where  $d_i$  and  $b_i$  are the flow-rates of the component  $i$  in the tops and bottoms,  $d_r$  and  $b_r$  are the flow-rates of the reference component in the tops and bottoms.

*Note:* from the column material balance:

$$d_i + b_i = f_i$$

where  $f_i$  is the flow rate of component  $i$  in the feed.

### **Minimum reflux ratio**

Colburn (1941) and Underwood (1948) have derived equations for estimating the minimum reflux ratio for multicomponent distillations. These equations are discussed in Volume 2, Chapter 11. As the Underwood equation is more widely used it is presented in this section. The equation can be stated in the form:

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1 \quad (11.60)$$

where  $\alpha_i$  = the relative volatility of component  $i$  with respect to some reference component, usually the heavy key,

$R_m$  = the minimum reflux ratio,

$x_{i,d}$  = concentration of component  $i$  in the tops at minimum reflux

and  $\theta$  is the root of the equation:

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q \quad (11.61)$$

where  $x_{i,f}$  = the concentration of component  $i$  in the feed, and  $q$  depends on the condition of the feed and was defined in Section 11.5.2.

The value of  $\theta$  must lie between the values of the relative volatility of the light and heavy keys, and is found by trial and error.

In the derivation of equations 11.60 and 11.61 the relative volatilities are taken as constant. The geometric average of values estimated at the top and bottom temperatures should be used. This requires an estimate of the top and bottom compositions. Though the compositions should strictly be those at minimum reflux, the values determined at total reflux, from the Fenske equation, can be used. A better estimate can be obtained by replacing the number of stages at total reflux in equation 11.59 by an estimate of the actual number; a value equal to  $N_m/0.6$  is often used. The Erbar-Maddox method of estimating the stage and reflux requirements, using the Fenske and Underwood equations, is illustrated in Example 11.7.

### **Feed-point location**

A limitation of the Erbar-Maddox, and similar empirical methods, is that they do not give the feed-point location. An estimate can be made by using the Fenske equation to calculate the number of stages in the rectifying and stripping sections separately, but this requires an estimate of the feed-point temperature. An alternative approach is to use the empirical equation given by Kirkbride (1944):

$$\log \left[ \frac{N_r}{N_s} \right] = 0.206 \log \left[ \left( \frac{B}{D} \right) \left( \frac{x_{f,\text{HK}}}{x_{f,\text{LK}}} \right) \left( \frac{x_{b,\text{LK}}}{x_{d,\text{HK}}} \right)^2 \right] \quad (11.62)$$

where  $N_r$  = number of stages above the feed, including any partial condenser,

$N_s$  = number of stages below the feed, including the reboiler,

$B$  = molar flow bottom product,

$D$  = molar flow top product,

$x_{f,\text{HK}}$  = concentration of the heavy key in the feed,

$x_{f,\text{LK}}$  = concentration of the light key in the feed,

$x_{d,\text{HK}}$  = concentration of the heavy key in the top product,

$x_{b,\text{LK}}$  = concentration of the light key if in the bottom product.

The use of this equation is illustrated in Example 11.8.

### **11.7.4. Distribution of non-key components (graphical method)**

The graphical procedure proposed by Hengstebeck (1946), which is based on the Fenske equation, is a convenient method for estimating the distribution of components between the top and bottom products.

Hengstebeck and Geddes (1958) have shown that the Fenske equation can be written in the form:

$$\log \left( \frac{d_i}{b_i} \right) = A + C \log \alpha_i \quad (11.63)$$

Specifying the split of the key components determines the constants  $A$  and  $C$  in the equation.

The distribution of the other components can be readily determined by plotting the distribution of the keys against their relative volatility on log-log paper, and drawing a straight line through these two points. The method is illustrated in Example 11.6.

Yaws *et al.* (1979) have shown that the components distributions calculated by equation 11.63 compare well with those obtained by rigorous plate by plate calculations.

Chang (1980) gives a computer program, based on the Geddes-Hengstebeck equation, for the estimation of component distributions.

### Example 11.6

Use the Geddes-Hengstebeck method to check the component distributions for the separation specified in Example 11.5

*Summary of problem, flow per 100 kmol feed*

Component	$\alpha_i$	Feed ( $f_i$ )	Distillate ( $d_i$ )	Bottoms ( $b_i$ )
C <sub>3</sub>	5	5		
iC <sub>4</sub>	2.6	15		
nC <sub>4</sub> (LK)	2.0	25	24	1
iC <sub>5</sub> (HK)	1.0	20	1	19
nC <sub>5</sub>	0.85	35		

### Solution

The average volatilities will be taken as those estimated in Example 11.5. Normally, the volatilities are estimated at the feed bubble point, which gives a rough indication of the average column temperatures. The dew point of the tops and bubble point of the bottoms can be calculated once the component distributions have been estimated, and the calculations repeated with a new estimate of the average relative volatilities, as necessary.

$$\text{For the light key, } \frac{d_i}{b_i} = \frac{24}{1} = 24$$

$$\text{For the heavy key, } \frac{d_i}{b_i} = \frac{1}{19} = 0.053$$

These values are plotted on Figure 11.12.

The distribution of the non-keys are read from Figure 11.12 at the appropriate relative volatility and the component flows calculated from the following equations:

Overall column material balance

$$f_i = d_i + b_i$$

from which

$$d_i = \frac{f_i}{\left(\frac{b_i}{d_i} + 1\right)}$$

$$b_i = \frac{f_i}{\left(\frac{d_i}{b_i} + 1\right)}$$



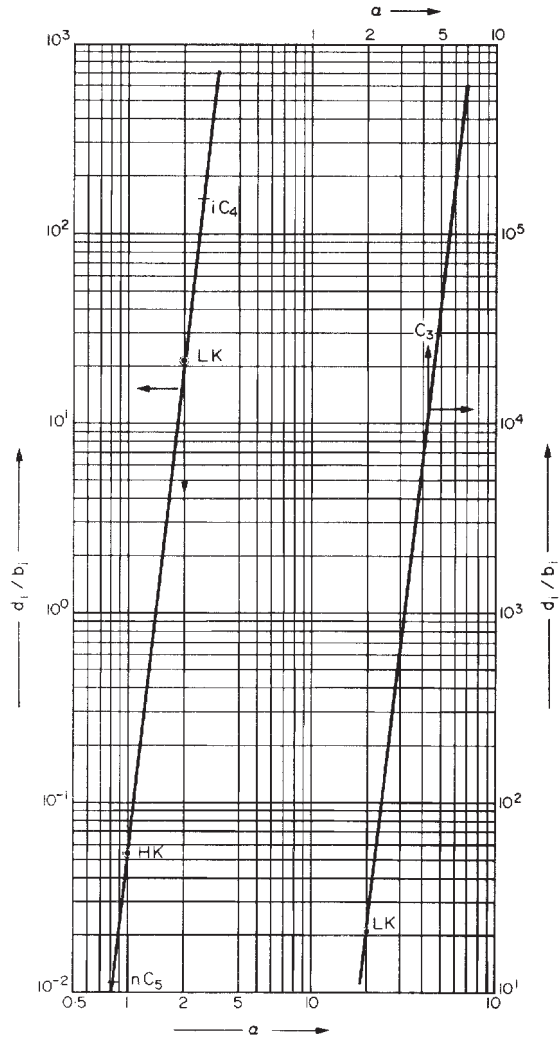


Figure 11.12. Component Distribution (Example 11.6)

	$\alpha_i$	$f_i$	$d_i/b_i$	$d_i$	$b_i$
C <sub>3</sub>	5	5	40,000	5	0
iC <sub>4</sub>	2.6	15	150	14.9	0.1
nC <sub>4</sub>	2.0	25	21	24	1
iC <sub>5</sub>	1.0	20	0.053	1	19
nC <sub>5</sub>	0.85	35	0.011	0.4	34.6

As these values are close to those assumed for the calculation of the dew points and bubble points in Example 11.5, there is no need to repeat with new estimates of the relative volatilities.

**Example 11.7**

For the separation specified in Example 11.5, evaluate the effect of changes in reflux ratio on the number of stages required. This is an example of the application of the Erbar-Maddox method.

**Solution**

The relative volatilities estimated in Example 11.5, and the component distributions calculated in Example 11.6 will be used for this example.

Summary of data				
	$\alpha_i$	$f_i$	$d_i$	$b_i$
C <sub>3</sub>	5	5	5	0
iC <sub>4</sub>	2.6	15	14.9	0.1
nC <sub>4</sub> (LK)	2.0	25	24	1
iC <sub>5</sub> (HK)	1	20	1	19
nC <sub>5</sub>	0.85	35	0.4	34.6
		100	$D = 45.3$	$B = 54.7$

Minimum number of stages; Fenske equation, equation 11.58:

$$N_m = \frac{\log \left[ \left( \frac{24}{1} \right) \left( \frac{19}{1} \right) \right]}{\log 2} = \underline{\underline{8.8}}$$

Minimum reflux ratio; Underwood equations 11.60 and 11.61.

This calculation is best tabulated.

As the feed is at its boiling point  $q = 1$

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 0 \quad (11.61)$$

$x_{i,f}$	$\alpha_i$	$\alpha_i x_{i,f}$	$\theta = 1.5$	Try	
				$\theta = 1.3$	$\theta = 1.35$
0.05	5	0.25	0.071	0.068	0.068
0.15	2.6	0.39	0.355	0.300	0.312
0.25	2.0	0.50	1.000	0.714	0.769
0.20	1	0.20	-0.400	-0.667	-0.571
0.35	0.85	0.30	-0.462	-0.667	-0.600
			$\Sigma = 0.564$	-0.252	0.022
					close enough

$\theta = 1.35$

Equation 11.60

$x_{i,d}$	$\alpha_i$	$\alpha_i x_{i,d}$	$\alpha_i x_{i,d} / (\alpha_i - \theta)$
0.11	5	0.55	0.15
0.33	2.6	0.86	0.69
0.53	2.0	1.08	1.66
0.02	1	0.02	-0.06
0.01	0.85	0.01	-0.02
			$\Sigma = 2.42$

$$R_m + 1 = 2.42$$

$$R_m = \underline{\underline{1.42}}$$

$$\frac{R_m}{(R_m + 1)} = \frac{1.42}{2.42} = 0.59$$

Specimen calculation, for  $R = 2.0$ 

$$\frac{R}{(R + 1)} = \frac{2}{3} = 0.66$$

from Figure 11.11

$$\frac{N_m}{N} = 0.56$$

$$N = \frac{8.8}{0.56} = \underline{\underline{15.7}}$$

for other reflux ratios

$R$	2	3	4	5	6
$N$	15.7	11.9	10.7	10.4	10.1

*Note:* Above a reflux ratio of 4 there is little change in the number of stages required, and the optimum reflux ratio will be near this value.

### Example 11.8

Estimate the position of the feed point for the separation considered in Example 11.7, for a reflux ratio of 3.

### Solution

Use the Kirkbride equation, equation 11.62. Product distributions taken from Example 11.6,

$$x_{b,\text{LK}} = \frac{1}{54.7} = 0.018$$

$$x_{d,\text{HK}} = \frac{1}{45.3} = 0.022$$

$$\log\left(\frac{N_r}{N_s}\right) = 0.206 \log\left[\frac{54.7}{45.3} \left(\frac{0.20}{0.25}\right) \left(\frac{0.018}{0.022}\right)^2\right]$$

$$\log\left(\frac{N_r}{N_s}\right) = 0.206 \log(0.65)$$

$$\frac{N_r}{N_s} = \underline{\underline{0.91}}$$

for  $R = 3$ ,  $N = 12$

number of stages, excluding the reboiler = 11

$$N_r + N_s = 11$$

$$N_s = 11 - N_r = 11 - 0.91N_s$$

$$N_s = \frac{11}{1.91} = 5.76, \text{ say } \underline{\underline{6}}$$

Checks with the method used in Example 11.5, where the reflux ratio was 2.5.

### Example 11.9

This example illustrates the complexity and trial and error nature of stage-by-stage calculation.

The same problem specification has been used in earlier examples to illustrate the shortcut design methods.

A butane-pentane splitter is to operate at 8.3 bar with the following feed composition:

		$x_f$	f mol/100 mol feed
Propane,	C <sub>3</sub>	0.05	5
Isobutane,	iC <sub>4</sub>	0.15	15
Normal butane,	nC <sub>4</sub>	0.25	25
Isopentane,	iC <sub>5</sub>	0.20	20
Normal pentane,	nC <sub>5</sub>	0.35	35
Light key	nC <sub>4</sub>		
Heavy key	iC <sub>5</sub>		

For a specification of not more than 1 mol of the light key in the bottom product and not more than 1 mol of the heavy key in the top product, and a reflux ratio of 2.5, make a stage-by-stage calculation to determine the product composition and number of stages required.

### Solution

Only sufficient trial calculations will be made to illustrate the method used. Basis 100 mol feed.

Estimation of dew and bubble points

$$\text{Bubble point } \sum y_i = \sum K_i x_i = 1.0 \quad (11.5a)$$

$$\text{Dew point } \sum x_i = \sum \frac{y_i}{K_i} = 1.0 \quad (11.5b)$$

The  $K$  values, taken from the De Priester charts (Chapter 8), are plotted in Figure (a) for easy interpolation.

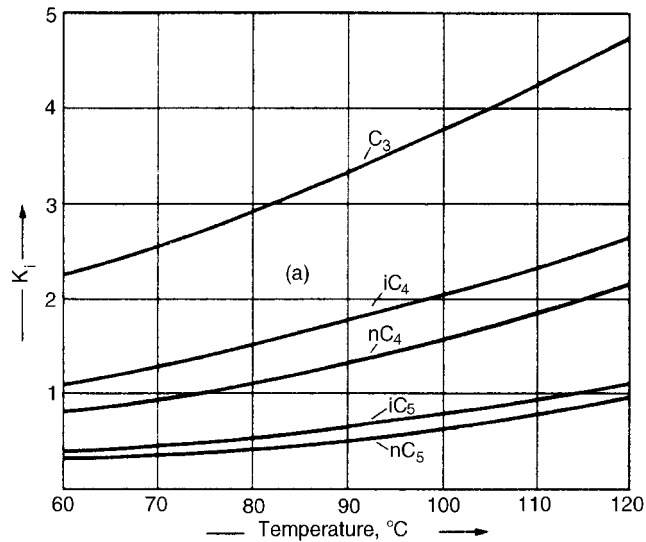


Figure (a).  $K$ -values at 8.3 bar

To estimate the dew and bubble points, assume that nothing heavier than the heavy key appears in the tops, and nothing lighter than the light key in the bottoms.

	$d$	$x_d$	$b$	$x_b$
C <sub>3</sub>	5	0.11	0	—
C <sub>4</sub>	15	0.33	0	—
nC <sub>4</sub>	24	0.54	1	0.02
iC <sub>5</sub>	1	0.02	19	0.34
nC <sub>5</sub>	0	—	35	0.64
	45		55	

Bubble-point calculation, bottoms

	$x_b$	Try 100°C		Try 120°C	
		$K_i$	$K_i x_i$	$K_i$	$K_i x_i$
C <sub>3</sub>	—	—	—	—	—
iC <sub>4</sub>	—	—	—	—	—
nC <sub>4</sub>	0.02	1.85	0.04	2.1	0.04
iC <sub>5</sub>	0.34	0.94	0.32	1.1	0.37
nC <sub>5</sub>	0.64	0.82	0.52	0.96	0.61
$\Sigma K_i x_i = 0.88$				1.02	
temp. too low				close enough	

Dew-point calculation, tops

	$x_d$	Try 70°C		Try 60°C	
		$K_i$	$y_i/K_i$	$K_i$	$y_i/K_i$
C <sub>3</sub>	0.11	2.6	0.04	2.20	0.24
iC <sub>4</sub>	0.33	1.3	0.25	1.06	0.35
nC <sub>4</sub>	0.54	0.9	0.60	0.77	0.42
iC <sub>5</sub>	0.02	0.46	0.04	0.36	0.01
nC <sub>5</sub>	—	—	—	—	—
$\Sigma y_i/K_i = 0.94$				1.02	
temp. too high				close enough	

Bubble-point calculation, feed (liquid feed)

	$x_f$	Try 80°C		Try 90°C		Try 85°C	
		$K_i$	$x_i K_i$	$K_i$	$x_i K_i$	$K_i$	$x_i K_i$
C <sub>3</sub>	0.05	2.9	0.15	3.4	0.17	3.15	0.16
iC <sub>4</sub>	0.15	1.5	0.23	1.8	0.27	1.66	0.25
nC <sub>4</sub>	0.25	1.1	0.28	1.3	0.33	1.21	0.30
iC <sub>5</sub>	0.20	0.5	0.11	0.66	0.13	0.60	0.12
nC <sub>5</sub>	0.35	0.47	0.16	0.56	0.20	0.48	0.17
		0.93		1.10		1.00	
		temp. too low		temp. too high		satisfactory	

**Stage-by-stage calculations**

Top down calculations, assume total condensation with no subcooling

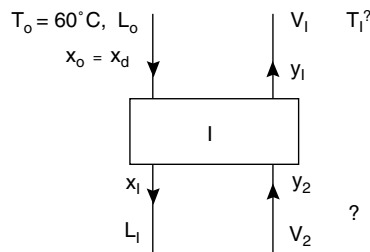
$$y_1 = x_d = x_0$$

It is necessary to estimate the composition of the “non-keys” so that they can be included in the stage calculations. As a first trial the following values will be assumed:

	$x_d$	$d$
C <sub>3</sub>	0.10	5
iC <sub>4</sub>	0.33	15
nC <sub>4</sub>	0.54	24
iC <sub>5</sub>	0.02	1
nC <sub>5</sub>	0.001	0.1
		45.1

In each stage calculation it will necessary to estimate the stage temperatures to determine the  $K$  values and liquid and vapour enthalpies. The temperature range from top to bottom of the column will be approximately  $120 - 60 = 60^\circ\text{C}$ . An approximate calculation (Example 11.7) has shown that around fourteen ideal stages will be needed; so the temperature change from stage to stage can be expected to be around 4 to  $5^\circ\text{C}$ .

### Stage 1



$$L_0 = R \times D = 2.5 \times 45.1 = 112.8$$

$$V_1 = (R + 1)D = 3.5 \times 45.1 = 157.9$$

Estimation of stage temperature and outlet liquid composition ( $x_1$ )

	$y_1$	Try $T_1 = 66^\circ\text{C}$		Try $T_1 = 65^\circ\text{C}$		$x_1 = y_i/K_i$ Normalised
		$K_i$	$y_i/K_i$	$K_i$	$y_i/K_i$	
C <sub>3</sub>	0.10	2.40	0.042	2.36	0.042	0.042
iC <sub>4</sub>	0.33	1.20	0.275	1.19	0.277	0.278
nC <sub>4</sub>	0.54	0.88	0.614	0.86	0.628	0.629
iC <sub>5</sub>	0.02	0.42	0.048	0.42	0.048	0.048
nC <sub>5</sub>	0.001	0.32	0.003	0.32	0.003	0.003
		$\Sigma y_i/K_i = 0.982$ too low		0.998 close enough		

## Summary of stage equations

$$L_0 + V_2 = L_1 + V_1 \quad (\text{i})$$

$$L_0x_0 + V_2y_2 = L_1x_1 + V_1y_1 \quad (\text{ii})$$

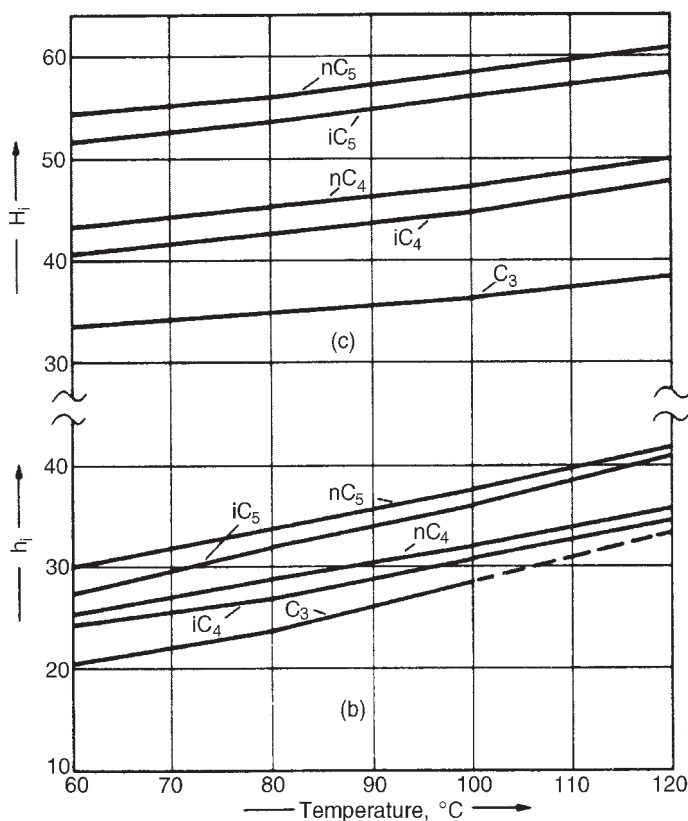
$$h_0L_0 + H_2V_2 = h_1L_1 + H_1V_1 \quad (\text{iii})$$

$$h = f(x, T) \quad (\text{iv})$$

$$H = f(x, T) \quad (\text{v})$$

The enthalpy relationship is plotted in Figures (b) and (c).

$$y_i = K_i x_i \quad (\text{vi})$$



Figures (b) and (c). Enthalpy kJ/mol (adapted from J. B. Maxwell, *Data Book of Hydrocarbons* (Van Nostrand, 1962))

Before a heat balance can be made to estimate  $L_1$  and  $V_2$ , an estimate of  $y_2$  and  $T_2$  is needed.  $y_2$  is dependent on the liquid and vapour flows, so as a first trial assume that



these are constant and equal to  $L_0$  and  $V_1$ ; then, from equations (i) and (ii),

$$y_2 = \left( \frac{L_0}{V_1} \right) (x_1 - x_0) + y_1$$

$$\frac{L_0}{V_1} = \frac{112.8}{157.9} = 0.71$$

	$x_1$	$x_0$	$y_2 = 0.71(x_1 - x_0) + y_1$	$y_2$ Normalised
C <sub>3</sub>	0.042	0.10	0.057	0.057
iC <sub>4</sub>	0.278	0.33	0.294	0.292
nC <sub>4</sub>	0.629	0.54	0.604	0.600
iC <sub>5</sub>	0.048	0.02	0.041	0.041
nC <sub>5</sub>	0.003	0.001	0.013	0.013
1.009				
close enough				

Enthalpy data from Figures (b) and (c) J/mol

	$h_0(T_0 = 60^\circ\text{C})$			$h_1(T_1 = 65^\circ\text{C})$		
	$x_0$	$h_i$	$h_i x_i$	$x_1$	$h_i$	$h_i x_i$
C <sub>3</sub>	0.10	20,400	2040	0.042	21,000	882
iC <sub>4</sub>	0.33	23,400	7722	0.278	24,900	6897
nC <sub>4</sub>	0.54	25,200	13,608	0.629	26,000	16,328
iC <sub>5</sub>	0.02	27,500	550	0.048	28,400	1363
nC <sub>5</sub>	0.001	30,000	30	0.003	30,700	92
$h_0 = 23,950$			$h_1 = 25,562$			
	$H_1(T_1 = 65^\circ\text{C})$			$H_2(T_2 = 70^\circ\text{C assumed})$		
	$v_1$	$H_i$	$H_i y_i$	$y_2$	$H_i$	$H_i y_i$
C <sub>3</sub>	0.10	34,000	3400	0.057	34,800	1984
iC <sub>4</sub>	0.33	41,000	13,530	0.292	41,300	12,142
nC <sub>4</sub>	0.54	43,700	23,498	0.600	44,200	26,697
iC <sub>5</sub>	0.02	52,000	1040	0.041	52,500	2153
nC <sub>5</sub>	0.001	54,800	55	0.013	55,000	715
$H_1 = 41,623$			$H_2 = 43,691$			

Energy balance (equation iii)

$$23,950 \times 112.8 + 43,691V_2 = 25,562L_1 + 41,623 \times 157.9$$

$$43,691V_2 = 255,626L_1 + 3,870,712$$

Material balance (equation i)

$$112.8 + V_2 = L_1 + 157.9$$

substituting

$$43,691(L_1 + 45.1) = 25,562L_1 + 3,870,712$$

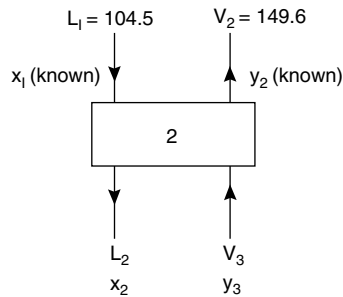
$$L_1 = 104.8$$

$$V_2 = 104.8 + 45.1 = 149.9$$

$$\frac{L_1}{V_2} = 0.70$$

Could revise calculated values for  $y_2$  but  $L_1/V_2$  is close enough to assumed value of 0.71, so there would be no significant difference from first estimate.

### Stage 2



Estimation of stage temperature and outlet liquid composition ( $x_2$ ).

$T_2 = 70^\circ\text{C}$ (use assumed value as first trial)				
	$y_2$	$K_i$	$x_2 = y_2/K_i$	$x_2$ Normalised
C <sub>3</sub>	0.057	2.55	0.022	0.022
iC <sub>4</sub>	0.292	1.30	0.226	0.222
nC <sub>4</sub>	0.600	0.94	0.643	0.630
iC <sub>5</sub>	0.041	0.43	0.095	0.093
nC <sub>5</sub>	0.013	0.38	0.034	0.033
			1.020	
			close enough to 1.0	

$$y_3 = \frac{L}{V}(x_2 - x_1) + y_2$$

As a first trial take  $L/V$  as  $L_1/V_1 = 0.70$

	$x_2$	$x_1$	$y_3 = 0.70(x_2 - x_1) + y_2$	$y_3$ Normalised
C <sub>3</sub>	0.022	0.042	0.044	0.043
iC <sub>4</sub>	0.222	0.277	0.256	0.251
nC <sub>4</sub>	0.630	0.628	0.613	0.601
iC <sub>5</sub>	0.093	0.048	0.072	0.072
nC <sub>5</sub>	0.033	0.003	0.035	0.034
			1.020	

Enthalpy data from Figures (b) and (c)

	$h_2(T_2 = 70^\circ\text{C})$			$H_3(T_3 = 75^\circ\text{C assumed})$		
	$x_2$	$h_i$	$h_i x_2$	$y_3$	$H_i$	$H_i y_3$
C <sub>3</sub>	0.022	21,900	482	0.043	34,600	1488
iC <sub>4</sub>	0.222	25,300	5617	0.251	41,800	10,492
nC <sub>4</sub>	0.630	27,000	17,010	0.601	44,700	26,865
iC <sub>5</sub>	0.093	29,500	2744	0.072	53,000	3816
nC <sub>5</sub>	0.033	31,600	1043	0.035	55,400	1939
		$h_2 = 26,896$			$H_3 = 44,600$	

Energy balance

$$25,562 \times 104.8 + 44,600V_3 = 4369 \times 149.9 + 26,896L_2$$

Material balance

$$104.8 + V_3 = 149.9 + L_2$$

$$L_2 = 105.0$$

$$V_3 = 150.1$$

$$\frac{L_2}{V_3} = 0.70 \text{ checks with assumed value.}$$

### Stage 3

As the calculated liquid and vapour flows are not changing much from stage to stage the calculation will be continued with the value of  $L/V$  taken as constant at 0.7.

Try $T_3 = 75^\circ\text{C}$ (assumed value)				
	$K_i$	$x_3 = y_3/K_i$	Normalised	$y_4 = 0.7(x_3 - x_2) + y_3$
C <sub>3</sub>	2.71	0.016	0.015	0.38
iC <sub>4</sub>	1.40	0.183	0.177	0.217
nC <sub>4</sub>	1.02	0.601	0.580	0.570
iC <sub>5</sub>	0.50	0.144	0.139	0.104
nC <sub>5</sub>	0.38	0.092	0.089	0.074
				1.036
Close enough				1.003

**Stage 4**

Try $T_4 = 81^\circ\text{C}$				
	$K_i$	$x_4 = y_4/K_i$	Normalised	$y_5 = 0.7(x_4 - x_3) + y_4$
C <sub>3</sub>	2.95	0.013	0.013	0.039
iC <sub>4</sub>	1.55	0.140	0.139	0.199
nC <sub>4</sub>	1.13	0.504	0.501	0.515
iC <sub>5</sub>	0.55	0.189	0.188	0.137
nC <sub>5</sub>	0.46	0.161	0.166	0.118
				1.007
Close enough				1.008

**Stage 5**

Try $T_5 = 85^\circ\text{C}$				
	$K_i$	$x_5$	Normalised	$y_6 = 0.7(x_5 - x_4) + y_5$
C <sub>3</sub>	3.12	0.013	0.012	0.038
iC <sub>4</sub>	1.66	0.120	0.115	0.179
nC <sub>4</sub>	1.20	0.430	0.410	0.450
iC <sub>5</sub>	0.60	0.228	0.218	0.159
nC <sub>5</sub>	0.46	0.257	0.245	0.192
				1.048
Close enough				1.018

**Stage 6**

	Try $T_6 = 90^\circ\text{C}$		Try $T_6 = 92^\circ\text{C}$			
	$K_i$	$x_6$	$K_i$	$x_6$	Normalised	$y_7$
C <sub>3</sub>	3.35	0.011	3.45	0.011	0.011	0.037
iC <sub>4</sub>	1.80	0.099	1.85	0.097	0.095	0.166
nC <sub>4</sub>	1.32	0.341	1.38	0.376	0.318	0.386
iC <sub>5</sub>	0.65	0.245	0.69	0.230	0.224	0.163
nC <sub>5</sub>	0.51	0.376	0.53	0.362	0.350	0.268
		1.072		1.026		1.020
		too low		close enough		

Note: ratio of LK to HK in liquid from this stage =  $\frac{0.386}{0.163} = 2.37$

**Stage 7**

Try $T_6 = 97^\circ\text{C}$			
	$K_i$	$x_7$	Normalised
C <sub>3</sub>	3.65	0.010	0.010
iC <sub>4</sub>	1.98	0.084	0.083
nC <sub>4</sub>	1.52	0.254	0.251
iC <sub>5</sub>	0.75	0.217	0.214
nC <sub>5</sub>	0.60	0.447	0.442
		1.012	

$$\text{ratio } \frac{\text{LK}}{\text{HK}} = \frac{0.251}{0.214} = 1.17$$

This is just below the ratio in the feed

$$= \frac{25}{20} = 1.25$$

So, the feed would be introduced at this stage.

But the composition of the non-key components on the plate does not match the feed composition.

	$x_f$	$x_7$
C <sub>3</sub>	0.05	0.10
iC <sub>4</sub>	0.15	0.084
nC <sub>4</sub>	0.25	0.254
iC <sub>5</sub>	0.20	0.217
nC <sub>5</sub>	0.35	0.447

So it would be necessary to adjust the assumed top composition and repeat the calculation.

**Bottom-up calculation**

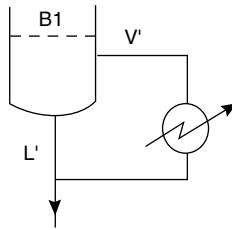
To illustrate the procedure the calculation will be shown for the reboiler and bottom stage, assuming constant molar overflow.

With the feed at its boiling point and constant molar overflow the base flows can be calculated as follows:

$$V' = V_0 = 157.9$$

$$L' = L_0 + \text{FEED} = 112.8 + 100 = 212.8$$

$$\frac{V'}{L'} = \frac{157.9}{212.8} = 0.74$$



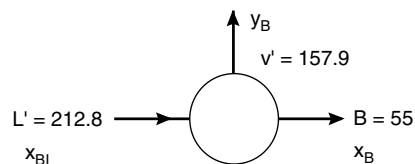
It will be necessary to estimate the concentration of the non-key components in the bottom product; as a first trial take:

$C_3$	$iC_4$	$nC_4$	$iC_5$	$nC_5$
0.001	0.001	0.02	0.34	0.64

Reboiler

Check bubble-point estimate of 120°C

	Try 120°C			Try 118°C	
	$x_B$	$K_i$	$y_B = K_i x_B$	$K_i$	$y_B$
$C_3$	0.001	4.73	0.005	4.60	0.005
$iC_4$	0.001	2.65	0.003	2.58	0.003
$nC_4$	0.02	2.10	0.042	2.03	0.041
$iC_5$	0.34	1.10	0.374	1.06	0.360
$nC_5$	0.64	0.96	0.614	0.92	0.589
			1.038		0.998
			too high		close enough



Material balance:

$$\begin{aligned}
 x_{B1}L' &= y_B V' + x_B B \\
 x_{B1} &= \frac{V'}{L'} y_B + \frac{B}{L'} x_B \\
 x_{B1} &= \frac{157.9}{212.8} y_B + \frac{55}{212.8} x_B \\
 &= 0.74 y_B + 0.26 x_B
 \end{aligned}$$

Stage 1 from base (B1)

	$x_B$	$y_B$	$x_{B1}$	$x_{B2} = 0.74(y_{1B} - y_B) + x_{1B}$
C <sub>3</sub>	0.001	0.005	0.004	0.014
iC <sub>4</sub>	0.001	0.003	0.002	0.036
nC <sub>4</sub>	0.02	0.041	0.020	0.019
iC <sub>5</sub>	0.34	0.361	0.356	0.357
nC <sub>5</sub>	0.64	0.590	0.603	0.559
				0.985

The calculation is continued stage-by-stage up the column to the feed point (stage 7 from the top). If the vapour composition at the feed point does not mesh with the top-down calculation, the assumed concentration of the non-keys in the bottom product is adjusted and the calculations repeated.

## 11.8. MULTICOMPONENT SYSTEMS: RIGOROUS SOLUTION PROCEDURES (COMPUTER METHODS)

The application of digital computers has made the rigorous solution of the MESH equations (Section 11.3.1) a practical proposition, and computer methods for the design of multicomponent separation columns will be available in most design organisations. Programs, and computer time, can also be rented from commercial computing bureaux. A considerable amount of work has been done over the past twenty or so years to develop efficient and reliable computer-aided design procedures for distillation and other staged processes. A detailed discussion of this work is beyond the scope of this book and the reader is referred to the specialist books that have been published on the subject, Smith (1963), Holland (1997) and Kister (1992), and to the numerous papers that have appeared in the chemical engineering literature. A good summary of the present state of the art is given by Haas (1992).

Several different approaches have been taken to develop programs that are efficient in the use of computer time, and suitable for the full range of multicomponent separation processes that are used in the process industries. A design group will use those methods that are best suited to the processes that it normally handles.

In this section only a brief outline of the methods that have been developed will be given.

The basic steps in any rigorous solution procedure will be:

1. Specification of the problem; complete specification is essential for computer methods.
2. Selection of values for the iteration variables; for example, estimated stage temperatures, and liquid and vapour flows (the column temperature and flow profiles).
3. A calculation procedure for the solution of the stage equations.
4. A procedure for the selection of new values for the iteration variables for each set of trial calculations.
5. A procedure to test for convergence; to check if a satisfactory solution has been achieved.

It is convenient to consider the methods available under the following four headings:

1. Lewis-Matheson method.
2. Thiele-Geddes method.
3. Relaxation methods.
4. Linear algebra methods.

### ***Rating and design methods***

With the exception of the Lewis-Matheson method, all the methods listed above require the specification of the number of stages below and above the feed point. They are therefore not directly applicable to design: where the designer wants to determine the number of stages required for a specified separation. They are strictly what are referred to as “rating methods”; used to determine the performance of existing, or specified, columns. Given the number of stages they can be used to determine product compositions. Iterative procedures are necessary to apply rating methods to the design of new columns. An initial estimate of the number of stages can be made using short-cut methods and the programs used to calculate the product compositions; repeating the calculations with revised estimates till a satisfactory design is obtained.

#### **11.8.1. Lewis-Matheson method**

The method proposed by Lewis and Matheson (1932) is essentially the application of the Lewis-Sorel method (Section 11.5.1) to the solution of multicomponent problems. Constant molar overflow is assumed and the material balance and equilibrium relationship equations are solved stage by stage starting at the top or bottom of the column, in the manner illustrated in Example 11.9. To define a problem for the Lewis-Matheson method the following variables must be specified, or determined from other specified variables:

- Feed composition, flow rate and condition.
- Distribution of the key components.
- One product flow.
- Reflux ratio.
- Column pressure.
- Assumed values for the distribution of the non-key components.



The usual procedure is to start the calculation at the top and bottom of the column and proceed toward the feed point. The initial estimates of the component distributions in the products are then revised and the calculations repeated until the compositions calculated from the top and bottom starts mesh, and match the feed at the feed point.

Efficient procedures for adjusting the compositions to achieve a satisfactory mesh at the feed point are given by Hengstebeck (1976).

In some computer applications of the method, where the assumption of constant molar overflow is not made, it is convenient to start the calculations by assuming flow and temperature profiles. The stage component compositions can then be readily determined and used to revise the profiles for the next iteration. With this modification the procedure is similar to the Thiele-Geddes method discussed in the next section.

In general, the Lewis-Matheson method has not been found to be an efficient procedure for computer solutions, other than for relatively straightforward problems. It is not suitable for problems involving multiple feeds, and side-streams, or where more than one column is needed.

The method is suitable for interactive programs run on programmable calculators and Personal Computers. Such programs can be "semi-manual" in operation: the computer solving the stage equations, while control of the iteration variables, and convergence is kept by the designer. As the calculations are carried out one stage at a time, only a relatively small computer memory is needed.

### 11.8.2. Thiele-Geddes method

Like the Lewis-Matheson method, the original method of Thiele and Geddes (1933) was developed for manual calculation. It has subsequently been adapted by many workers for computer applications. The variables specified in the basic method, or that must be derived from other specified variables, are:

Reflux temperature.

Reflux flow rate.

Distillate rate.

Feed flows and condition.

Column pressure.

Number of equilibrium stages above and below the feed point.

The basic procedure used in the Thiele-Geddes method, with examples, is described in books by Smith (1963) and Deshpande (1985). The application of the method to computers is covered in a series of articles by Lyster *et al.* (1959) and Holland (1963).

The method starts with an assumption of the column temperature and flow profiles. The stage equations are then solved to determine the stage component compositions and the results used to revise the temperature profiles for subsequent trial calculations. Efficient convergence procedures have been developed for the Thiele-Geddes method. The so-called "theta method", described by Lyster *et al.* (1959) and Holland (1963), is recommended. The Thiele-Geddes method can be used for the solution of complex distillation problems,

and for other multi-component separation processes. A series of programs for the solution of problems in distillation, extraction, stripping and absorption, which use an iterative procedure similar to the Thiele-Geddes method, are given by Hanson *et al.* (1962).

### 11.8.3. Relaxation methods

With the exception of this method, all the methods described solve the stage equations for the steady-state design conditions. In an operating column other conditions will exist at start-up, and the column will approach the “design” steady-state conditions after a period of time. The stage material balance equations can be written in a finite difference form, and procedures for the solution of these equations will model the unsteady-state behaviour of the column.

Rose *et al.* (1958) and Hanson and Sommerville (1963) have applied “relaxation methods” to the solution of the unsteady-state equations to obtain the steady-state values. The application of this method to the design of multistage columns is described by Hanson and Sommerville (1963). They give a program listing and worked examples for a distillation column with side-streams, and for a reboiled absorber.

Relaxation methods are not competitive with the “steady-state” methods in the use of computer time, because of slow convergence. However, because they model the actual operation of the column, convergence should be achieved for all practical problems. The method has the potential of development for the study of the transient behaviour of column designs, and for the analysis and design of batch distillation columns.

### 11.8.4. Linear algebra methods

The Lewis-Matheson and Thiele-Geddes methods use a stage-by-stage procedure to solve the equations relating the component compositions to the column temperature and flow profiles. However, the development of high-speed digital computers with large memories makes possible the simultaneous solution of the complete set of MESH equations that describe the stage compositions throughout the column.

If the equilibrium relationships and flow-rates are known (or assumed) the set of material balance equations for each component is linear in the component compositions. Amundson and Pontinen (1958) developed a method in which these equations are solved simultaneously and the results used to provide improved estimates of the temperature and flow profiles. The set of equations can be expressed in matrix form and solved using the standard inversion routines available in modern computer systems. Convergence can usually be achieved after a few iterations.

This approach has been further developed by other workers; notably Wang and Henke (1966) and Naphtali and Sandholm (1971).

The linearisation method of Naphtali and Sandholm has been used by Fredenslund *et al.* (1977) for the multicomponent distillation program given in their book. Included in their book, and coupled to the distillation program, are methods for estimation of the liquid-vapour relationships (activity coefficients) using the UNIFAC method (see Chapter 8, Section 16.3). This makes the program particularly useful for the design of columns for

new processes, where experimental data for the equilibrium relationships are unlikely to be available. The program is recommended to those who do not have access to their own “in house” programs.

## 11.9. OTHER DISTILLATION SYSTEMS

### 11.9.1. Batch distillation

In batch distillation the mixture to be distilled is charged as a batch to the still and the distillation carried out till a satisfactory top or bottom product is achieved. The still usually consists of a vessel surmounted by a packed or plate column. The heater may be incorporated in the vessel or a separate reboiler used. Batch distillation should be considered under the following circumstances:

1. Where the quantity to be distilled is small.
2. Where a range of products has to be produced.
3. Where the feed is produced at irregular intervals.
4. Where the feed composition varies over a wide range.

Where the choice between batch and continuous is uncertain an economic evaluation of both systems should be made.

Batch distillation is an unsteady state process, the composition in the still (bottoms) varying as the batch is distilled.

Two modes of operation are used.

1. Fixed reflux, where the reflux rate is kept constant. The compositions will vary as the more volatile component is distilled off, and the distillation stopped when the average composition of the distillate collected, or the bottoms left, meet the specification required.
2. Variable reflux, where the reflux rate is varied throughout the distillation to produce a fixed overhead composition. The reflux ratio will need to be progressively increased as the fraction of the more volatile component in the base of the still decreases.

The basic theory of batch distillation is given in Volume 2, Chapter 11 and in several other texts: Hart (1997), Perry *et al.* (1997) and Walas (1990). In the simple theoretical analysis of batch distillation columns the liquid hold-up in the column is usually ignored. This hold-up can have a significant effect on the separating efficiency and should be taken into account when designing batch distillation columns. The practical design of batch distillation columns is covered by Hengstebeck (1976), Ellerbe (1997) and Hart (1997).

### 11.9.2. Steam distillation

In steam distillation, steam is introduced into the column to lower the partial pressure of the volatile components. It is used for the distillation of heat sensitive products and for compounds with a high boiling point. It is an alternative to vacuum distillation. The products must be immiscible with water. Some steam will normally be allowed to condense to provide the heat required for the distillation. Live steam can be injected

directly into the column base, or the steam generated by a heater in the still or in an external boiler.

The design procedures for columns employing steam distillation is essentially the same as that for conventional columns, making allowance for the presence of steam in the vapour; see Volume 2, Chapter 11.

Steam distillation is used extensively in the extraction of essential oils from plant materials.

### 11.9.3. Reactive distillation

Reactive distillation is the name given to the process where the chemical reaction and product separation are carried out simultaneously in one unit. Carrying out the reaction, with separation and purification of the product by distillation, gives the following advantages:

1. Chemical equilibrium restrictions are overcome, as the product is removed as it is formed.
2. Energy savings can be obtained, as the heat of reaction can be utilised for the distillation.
3. Capital costs are reduced, as only one vessel is required.

The design of reactive distillation columns is complicated by the complex interactions between the reaction and separation processes. A comprehensive discussion of the process is given by Sundmacher and Kiene (2003).

Reactive distillation is used in the production of MTBE (methyl tertiary butyl ether) and methyl acetate.

## 11.10. PLATE EFFICIENCY

The designer is concerned with real contacting stages; not the theoretical equilibrium stage assumed for convenience in the mathematical analysis of multistage processes. Equilibrium will rarely be attained in a real stage. The concept of a stage efficiency is used to link the performance of practical contacting stages to the theoretical equilibrium stage.

Three principal definitions of efficiency are used:

1. Murphree plate efficiency (Murphree, 1925), defined in terms of the vapour compositions by:

$$E_{mV} = \frac{y_n - y_{n-1}}{y_e - y_{n-1}} \quad (11.64)$$

where  $y_e$  is the composition of the vapour that would be in equilibrium with the liquid leaving the plate. The Murphree plate efficiency is the ratio of the actual separation achieved to that which would be achieved in an equilibrium stage (see Figure 11.6). In this definition of efficiency the liquid and the vapour stream are taken to be perfectly mixed; the compositions in equation 11.64 are the average composition values for the streams.

2. Point efficiency (Murphree point efficiency). If the vapour and liquid compositions are taken at a point on the plate, equation 11.64 gives the local or point efficiency,  $E_{mv}$ .

3. Overall column efficiency. This is sometimes confusingly referred to as the overall plate efficiency.

$$E_o = \frac{\text{number of ideal stages}}{\text{number of real stages}} \quad (11.65)$$

An estimate of the overall column efficiency will be needed when the design method used gives an estimate of the number of ideal stages required for the separation.

In some methods, the Murphree plate efficiencies can be incorporated into the procedure for calculating the number of stages and the number of real stages determined directly.

For the idealised situation where the operating and equilibrium lines are straight, the overall column efficiency and the Murphree plate efficiency are related by an equation derived by Lewis (1936):

$$E_o = \frac{\log \left[ 1 + E_{mV} \left( \frac{mV}{L} - 1 \right) \right]}{\log \left( \frac{mV}{L} \right)} \quad (11.66)$$

where  $m$  = slope of the equilibrium line,

$V$  = molar flow rate of the vapour,

$L$  = molar flow rate of the liquid.

Equation 11.66 is not of much practical use in distillation, as the slopes of the operating and equilibrium lines will vary throughout the column. It can be used by dividing the column into sections and calculating the slopes over each section. For most practical purposes, providing the plate efficiency does not vary too much, a simple average of the plate efficiency calculated at the column top, bottom and feed points will be sufficiently accurate.

### 11.10.1. Prediction of plate efficiency

Whenever possible the plate efficiencies used in design should be based on experimental values for similar systems, obtained on full-sized columns. There is no entirely satisfactory method for predicting plate efficiencies from the system physical properties and plate design parameters. However, the methods given in this section can be used to make a rough estimate where no reliable experimental values are available. They can also be used to extrapolate data obtained from small-scale experimental columns. If the system properties are at all unusual, experimental confirmation of the predicted values should always be obtained. The small, laboratory scale, glass sieve plate column developed by Oldershaw (1941) has been shown to give reliable values for scale-up. The use of Oldershaw columns is described in papers by Swanson and Gester (1962), Veatch *et al.* (1960) and Fair *et al.* (1983).

Some typical values of plate efficiency for a range of systems are given in Table 11.1. More extensive compilations of experimental data are given by Vital *et al.* (1984) and Kister (1992).

Plate, and overall column, efficiencies will normally be between 30 per cent and 70 per cent, and as a rough guide a figure of 50 per cent can be assumed for preliminary designs.

Table 11.1. Representative efficiencies, sieve plates

System	Column dia., m	Pressure kPa, abs	Efficiency %	
			$E_{mV}$	$E_o$
Water-methanol	1.0	—	80	
Water-ethanol	0.2	101	90	
Water-isopropanol	—	—		70
Water-acetone	0.15	90	80	
Water-acetic acid	0.46	101	75	
Water-ammonia	0.3	101	90	
Water-carbon dioxide	0.08	—	80	
Toluene-propanol	0.46	—	65	
Toluene-ethylene dichloride	0.05	101		75
Toluene-methylethylketone	0.15	—		85
Toluene-cyclohexane	2.4	—		70
Toluene-methylcyclohexane	—	27		90
Toluene-octane	0.15	101		40
Heptane-cyclohexane	1.2	165	95	85
	2.4	165		75
Propane-butane	—	—		100
Isobutane-n-butane	—	2070		110
Benzene-toluene	0.13	—	75	
Benzene-methanol	0.18	690	94	
Benzene-propanol	0.46	—	55	
Ethylbenzene-styrene	—	—	75	

$E_{mV}$  = Murphree plate efficiency,  
 $E_o$  = Overall column efficiency.

Efficiencies will be lower for vacuum distillations, as low weir heights are used to keep the pressure drop small (see Section 11.10.4).

### **Multicomponent systems**

The prediction methods given in the following sections, and those available in the open literature, are invariably restricted to binary systems. It is clear that in a binary system the efficiency obtained for each component must be the same. This is not so for a multicomponent system; the heavier components will usually exhibit lower efficiencies than the lighter components.

The following guide rules, adapted from a paper by Toor and Burchard (1960), can be used to estimate the efficiencies for a multicomponent system from binary data:

1. If the components are similar, the multicomponent efficiencies will be similar to the binary efficiency.
2. If the predicted efficiencies for the binary pairs are high, the multicomponent efficiency will be high.
3. If the resistance to mass transfer is mainly in the liquid phase, the difference between the binary and multicomponent efficiencies will be small.
4. If the resistance is mainly in the vapour phase, as it normally will be, the difference between the binary and multicomponent efficiencies can be substantial.

The prediction of efficiencies for multicomponent systems is also discussed by Chan and Fair (1984b). For mixtures of dissimilar compounds the efficiency can be very different

from that predicted for each binary pair, and laboratory or pilot-plant studies should be made to confirm any predictions.

### 11.10.2. O'Connell's correlation

A quick estimate of the overall column efficiency can be obtained from the correlation given by O'Connell (1946), which is shown in Figure 11.13. The overall column efficiency is correlated with the product of the relative volatility of the light key component (relative to the heavy key) and the molar average viscosity of the feed, estimated at the average column temperature. The correlation was based mainly on data obtained with hydrocarbon systems, but includes some values for chlorinated solvents and water-alcohol mixtures. It has been found to give reliable estimates of the overall column efficiency for hydrocarbon systems; and can be used to make an approximate estimate of the efficiency for other systems. The method takes no account of the plate design parameters; and includes only two physical property variables.

Eduljee (1958) has expressed the O'Connell correlation in the form of an equation:

$$E_o = 51 - 32.5 \log(\mu_a \alpha_a) \quad (11.67)$$

where  $\mu_a$  = the molar average liquid viscosity, mNs/m<sup>2</sup>,  
 $\alpha_a$  = average relative volatility of the light key.

### Absorbers

O'Connell gave a similar correlation for the *plate efficiency* of absorbers; Figure 11.14. Appreciably lower plate efficiencies are obtained in absorption than in distillation.

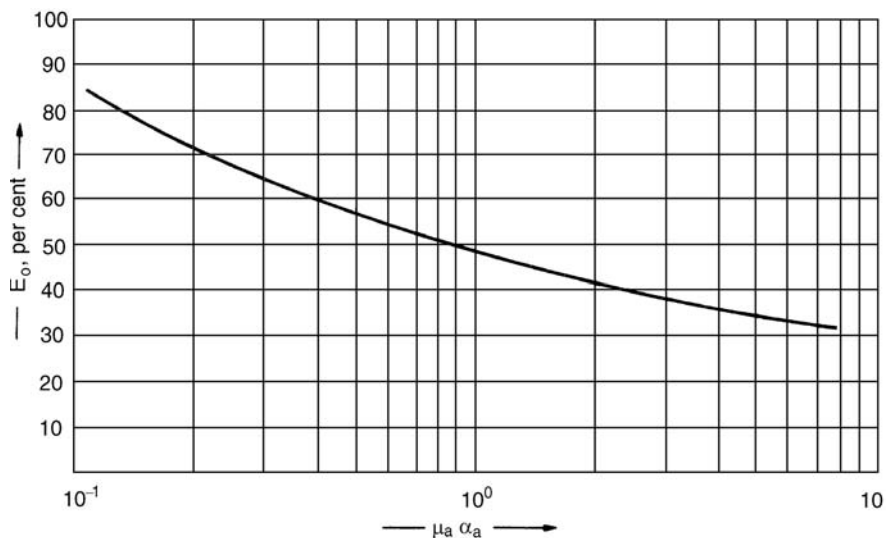


Figure 11.13. Distillation column efficiencies (bubble-caps) (after O'Connell, 1946)

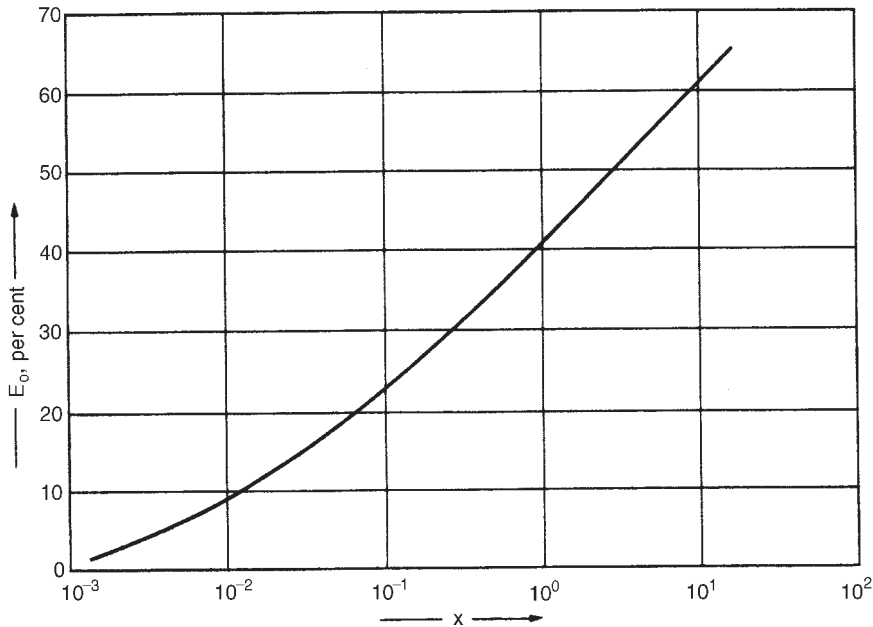


Figure 11.14. Absorber column efficiencies (bubble-caps) (after O'Connell, 1946)

In O'Connell's paper, the plate efficiency is correlated with a function involving Henry's constant, the total pressure, and the solvent viscosity at the operating temperature.

To convert the original data to SI units, it is convenient to express this function in the following form:

$$x = 0.062 \left[ \frac{\rho_s P}{\mu_s \mathcal{H} M_s} \right] = 0.062 \left[ \frac{\rho_s}{\mu_s K M_s} \right] \quad (11.68)$$

where  $\mathcal{H}$  = the Henry's law constant,  $\text{Nm}^{-2}/\text{mol fraction}$ ,

$P$  = total pressure,  $\text{N/m}^2$ ,

$\mu_s$  = solvent viscosity,  $\text{mNs/m}^2$ ,

$M_s$  = molecular weight of the solvent,

$\rho_s$  = solvent density,  $\text{kg/m}^3$ ,

$K$  = equilibrium constant for the solute.

### Example 11.10

Using O'Connell's correlation, estimate the overall column efficiency and the number of real stages required for the separation given in Example 11.5.

### Solution

From Example 11.5, feed composition, mol fractions:

propane 0.05, i-butane 0.15, n-butane 0.25, i-pentane 0.20, n-pentane 0.35.



Column-top temperature 65°C, bottom temperature 120°C.

Average relative volatility light key = 2.0

Take the viscosity at the average column temperature, 93°C,

viscosities, propane = 0.03 mNs/m<sup>2</sup>

butane = 0.12 mNs/m<sup>2</sup>

pentane = 0.14 mNs/m<sup>2</sup>

For feed composition, molar average viscosity =  $0.03 \times 0.05 + 0.12(0.15 + 0.25)$   
 $+ 0.14(0.20 + 0.35)$

$$= 0.13 \text{ mNs/m}^2$$

$$\alpha_a \mu_a = 2.0 \times 0.13 = 0.26$$

From Figure 11.13,  $E_o = \underline{70}$  per cent

From Example 11.4, number of ideal stages = 12, one ideal stage will be the reboiler, so number of actual stages

$$= \frac{(12 - 1)}{0.7} = \underline{\underline{16}}$$

### 11.10.3. Van Winkle's correlation

Van Winkle *et al.* (1972) have published an empirical correlation for the plate efficiency which can be used to predict plate efficiencies for binary systems. Their correlation uses dimensionless groups that include those system variables and plate parameters that are known to affect plate efficiency. They give two equations, the simplest, and that which they consider the most accurate, is given below. The data used to derive the correlation covered both bubble-cap and sieve plates.

$$E_{mV} = 0.07Dg^{0.14}Sc^{0.25}Re^{0.08} \quad (11.69)$$

where  $Dg$  = surface tension number =  $(\sigma_L/\mu_L u_v)$ ,

$u_v$  = superficial vapour velocity,

$\sigma_L$  = liquid surface tension,

$\mu_L$  = liquid viscosity,

$Sc$  = liquid Schmidt number =  $(\mu_L/\rho_L D_{LK})$ ,

$\rho_L$  = liquid density,

$D_{LK}$  = liquid diffusivity, light key component,

$Re$  = Reynolds number =  $(h_w u_v \rho_v / \mu_L \text{ (FA)})$ ,

$h_w$  = weir height,

$\rho_v$  = vapour density,

$$\text{(FA)} = \text{fractional area} = \frac{\text{(area of holes or risers)}}{\text{(total column cross-sectional area)}}$$

The use of this method is illustrated in Example 11.13.

### 11.10.4. AIChE method

This method of predicting plate efficiency, published in 1958, was the result of a five-year study of bubble-cap plate efficiency directed by the Research Committee of the American Institute of Chemical Engineers.

The AIChE method is the most detailed method for predicting plate efficiencies that is available in the open literature. It takes into account all the major factors that are known to affect plate efficiency; this includes:

- The mass transfer characteristics of the liquid and vapour phases.
- The design parameters of the plate.
- The vapour and liquid flow-rates.
- The degree of mixing on the plate.

The method is well established, and in the absence of experimental values, or proprietary prediction methods, should be used when more than a rough estimate of efficiency is needed.

The approach taken is semi-empirical. Point efficiencies are estimated making use of the “two-film theory”, and the Murphree efficiency estimated allowing for the degree of mixing likely to be obtained on real plates.

The procedure and equations are given in this section without discussion of the theoretical basis of the method. The reader should refer to the AIChE manual, AIChE (1958); or to Smith (1963) who gives a comprehensive account of the method, and extends its use to sieve plates. A brief discussion of the method is given in Volume 2; to which reference can be made for the definition of any unfamiliar terms used in the equations.

Chan and Fair (1984a) have published an alternative method for point efficiencies on sieve plates which they demonstrate gives closer predictions than the AIChE method.

### AIChE method

The mass transfer resistances in the vapour and liquid phases are expressed in terms of the number of transfer units,  $N_G$  and  $N_L$ . The point efficiency is related to the number of transfer units by the equation:

$$\frac{1}{\ln(1 - E_{mv})} = - \left[ \frac{1}{N_G} + \frac{mV}{L} \times \frac{1}{N_L} \right] \quad (11.70)$$

where  $m$  is the slope of the operating line and  $V$  and  $L$  the vapour and liquid molar flow rates.

Equation 11.70 is plotted in Figure 11.15.

The number of gas phase transfer units is given by:

$$N_G = \frac{(0.776 + 4.57 \times 10^{-3} h_w - 0.24 F_v + 105 L_p)}{\left( \frac{\mu_v}{\rho_v D_v} \right)^{0.5}} \quad (11.71)$$

where  $h_w$  = weir height, mm,

$F_v$  = the column vapour “ $F$ ” factor =  $u_a \sqrt{\rho_v}$ ,

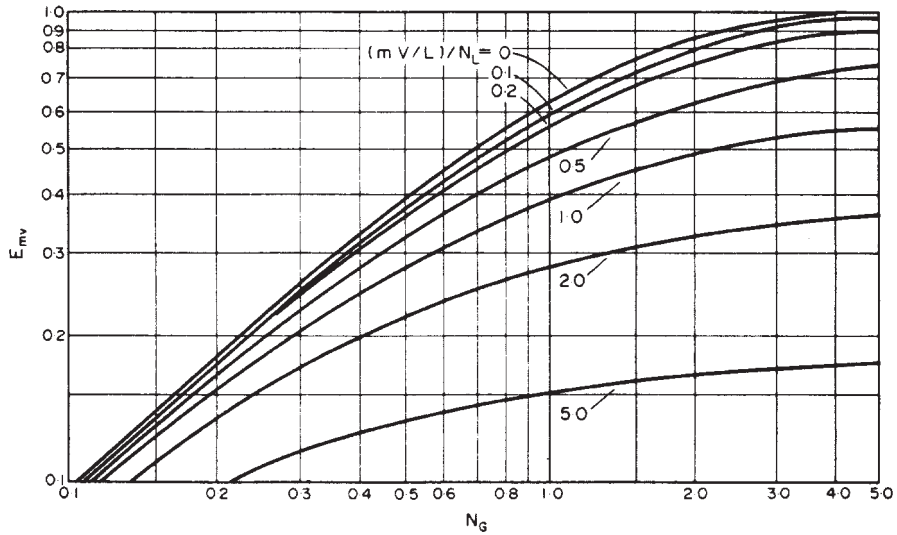


Figure 11.15. Relationship between point efficiency and number of liquid and vapour transfer units (Equation 11.70)

$u_a$  = vapour velocity based on the active tray area (bubbling area), see Section 11.13.2, m/s,

$L_p$  = the volumetric liquid flow rate across the plate, divided by the average width of the plate,  $\text{m}^3/\text{sm}$ . The average width can be calculated by dividing the active area by the length of the liquid path  $Z_L$ ,

$\mu_v$  = vapour viscosity,  $\text{Ns}/\text{m}^2$ ,

$\rho_v$  = vapour density;  $\text{kg}/\text{m}^3$ ,

$D_v$  = vapour diffusivity,  $\text{m}^2/\text{s}$ .

The number of liquid phase transfer units is given by:

$$N_L = (4.13 \times 10^8 D_L)^{0.5} (0.21 F_v + 0.15) t_L \quad (11.72)$$

where  $D_L$  = liquid phase diffusivity,  $\text{m}^2/\text{s}$ ,

$t_L$  = liquid contact time, s,

given by:

$$t_L = \frac{Z_c Z_L}{L_p} \quad (11.73)$$

where  $Z_L$  = length of the liquid path, from inlet downcomer to outlet weir, m,

$Z_c$  = liquid hold-up on the plate,  $\text{m}^3$  per  $\text{m}^2$  active area,

given by:

for bubble-cap plates

$$Z_c = 0.042 + 0.19 \times 10^{-3} h_w - 0.014 F_v + 2.5 L_p \quad (11.74)$$

for sieve plates

$$Z_c = 0.006 + 0.73 \times 10^{-3} h_w - 0.24 \times 10^{-3} F_v h_w + 1.22 L_p \quad (11.75)$$

The Murphree efficiency  $E_{mV}$  is only equal to the point efficiency  $E_{mv}$  if the liquid on the plate is perfectly mixed. On a real plate this will not be so, and to estimate the plate efficiency from the point efficiency some means of estimating the degree of mixing is needed. The dimensionless Peclet number characterises the degree of mixing in a system. For a plate the Peclet number is given by:

$$Pe = \frac{Z_L^2}{D_e t_L} \quad (11.76)$$

where  $D_e$  is the “eddy diffusivity”,  $m^2/s$ .

A Peclet number of zero indicates perfect mixing and a value of  $\infty$  indicates plug flow. For bubble-cap and sieve plates the eddy diffusivity can be estimated from the equation:

$$D_e = (0.0038 + 0.017 u_a + 3.86 L_p + 0.18 \times 10^{-3} h_w)^2 \quad (11.77)$$

The relation between the plate efficiency and point efficiency with the Peclet number as a parameter is shown in Figure 11.16a and b. The application of the AIChE method is illustrated in Example 11.12.

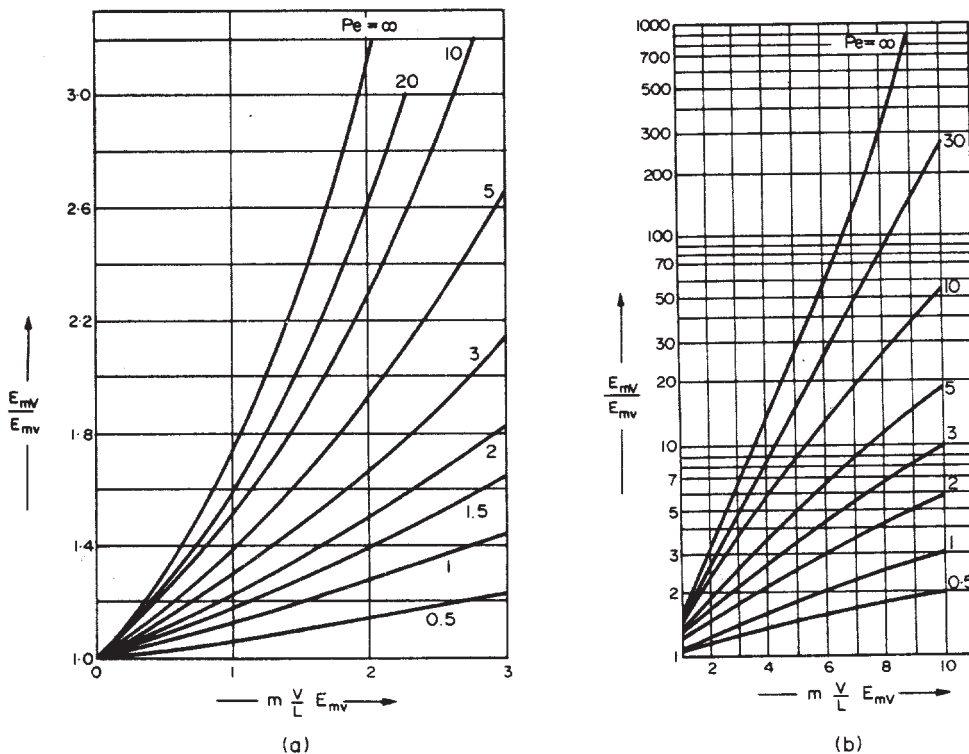


Figure 11.16. Relationship between plate and point efficiency

### **Estimation of physical properties**

To use the AIChE method, and Van Winkle's correlation, estimates of the physical properties are required. It is unlikely that experimental values will be found in the literature for all systems that are of practical interest. The prediction methods given in Chapter 8, and in the references given in that chapter, can be used to estimate values.

The AIChE design manual recommends the Wilke and Chang (1955) equation for liquid diffusivities and the Wilke and Lee (1955) modification to the Hirschfelder, Bird and Spotz equation for gas diffusivities.

### **Plate design parameters**

The significance of the weir height in the AIChE equations should be noted. The weir height was the plate parameter found to have the most significant effect on plate efficiency. Increasing weir height will increase the plate efficiency, but at the expense of an increase in pressure drop and entrainment. Weir heights will normally be in the range 40 to 100 mm for columns operating at and above atmospheric pressure, but will be as low as 6 mm for vacuum columns. This, in part, accounts for the lower plate efficiencies obtained in vacuum columns.

The length of the liquid path  $Z_L$  is taken into account when assessing the plate-mixing performance. The mixing correlation given in the AIChE method was not tested on large-diameter columns, and Smith (1963) states that the correlation should not be used for large-diameter plates. However, on a large plate the liquid path will normally be subdivided, and the value of  $Z_L$  will be similar to that in a small column.

The vapour "F" factor  $F_v$  is a function of the active tray area. Increasing  $F_v$  decreases the number of gas-phase transfer units. The liquid flow term  $L_p$  is also a function of the active tray area, and the liquid path length. It will only have a significant effect on the number of transfer units if the path length is long. In practice the range of values for  $F_v$ , the active area, and the path length will be limited by other plate design considerations.

### **Multicomponent systems**

The AIChE method was developed from measurements on binary systems. The AIChE manual should be consulted for advice on its application to multicomponent systems.

#### **11.10.5. Entrainment**

The AIChE method, and that of Van Winkle, predict the "dry" Murphree plate efficiency. In operation some liquid droplets will be entrained and carried up the column by the vapour flow, and this will reduce the actual, operating, efficiency.

The dry-plate efficiency can be corrected for the effects of entrainment using the equation proposed by Colburn (1936):

$$E_a = \frac{E_{mV}}{1 + E_{mV} \left[ \frac{\psi}{1 - \psi} \right]} \quad (11.78)$$

where  $E_a$  = actual plate efficiency, allowing for entrainment,

$$\psi = \text{the fractional entrainment} = \frac{\text{entrained liquid}}{\text{gross liquid flow}}.$$

Methods for predicting the entrainment from sieve plates are given in Section 11.13.5, Figure 11.27; a similar method for bubble-cap plates is given by Bolles (1963).

### 11.11. APPROXIMATE COLUMN SIZING

An approximate estimate of the overall column size can be made once the number of real stages required for the separation is known. This is often needed to make a rough estimate of the capital cost for project evaluation.

#### **Plate spacing**

The overall height of the column will depend on the plate spacing. Plate spacings from 0.15 m (6 in.) to 1 m (36 in.) are normally used. The spacing chosen will depend on the column diameter and operating conditions. Close spacing is used with small-diameter columns, and where head room is restricted; as it will be when a column is installed in a building. For columns above 1 m diameter, plate spacings of 0.3 to 0.6 m will normally be used, and 0.5 m (18 in.) can be taken as an initial estimate. This would be revised, as necessary, when the detailed plate design is made.

A larger spacing will be needed between certain plates to accommodate feed and side-streams arrangements, and for manways.

#### **Column diameter**

The principal factor that determines the column diameter is the vapour flow-rate. The vapour velocity must be below that which would cause excessive liquid entrainment or a high-pressure drop. The equation given below, which is based on the well-known Souders and Brown equation, Lowenstein (1961), can be used to estimate the maximum allowable superficial vapour velocity, and hence the column area and diameter,

$$\hat{u}_v = (-0.171l_t^2 + 0.27l_t - 0.047) \left[ \frac{(\rho_L - \rho_v)}{\rho_v} \right]^{1/2} \quad (11.79)$$

where  $\hat{u}_v$  = maximum allowable vapour velocity, based on the gross (total) column cross-sectional area, m/s,

$l_t$  = plate spacing, m, (range 0.5–1.5).

The column diameter,  $D_c$ , can then be calculated:

$$D_c = \sqrt{\frac{4\hat{V}_w}{\pi\rho_v\hat{u}_v}} \quad (11.80)$$

where  $\hat{V}_w$  is the maximum vapour rate, kg/s.

This approximate estimate of the diameter would be revised when the detailed plate design is undertaken.

### 11.12. PLATE CONTACTORS

Cross-flow plates are the most common type of plate contactor used in distillation and absorption columns. In a cross-flow plate the liquid flows across the plate and the vapour

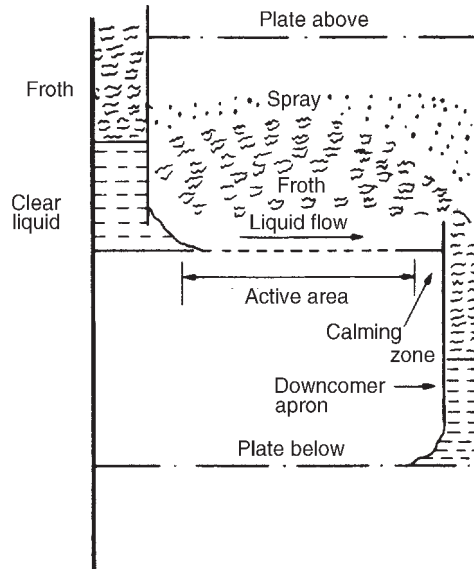


Figure 11.17. Typical cross-flow plate (sieve)

up through the plate. A typical layout is shown in Figure 11.17. The flowing liquid is transferred from plate to plate through vertical channels called “downcomers”. A pool of liquid is retained on the plate by an outlet weir.

Other types of plate are used which have no downcomers (non-cross-flow plates), the liquid showering down the column through large openings in the plates (sometimes called shower plates). These, and, other proprietary non-cross-flow plates, are used for special purposes, particularly when a low-pressure drop is required.

Three principal types of cross-flow tray are used, classified according to the method used to contact the vapour and liquid.

### **1. Sieve plate (perforated plate) (Figure 11.18)**

This is the simplest type of cross-flow plate. The vapour passes up through perforations in the plate; and the liquid is retained on the plate by the vapour flow. There is no positive vapour liquid seal, and at low flow-rates liquid will “weep” through the holes, reducing the plate efficiency. The perforations are usually small holes, but larger holes and slots are used.

### **2. Bubble-cap plates (Figure 11.19)**

In which the vapour passes up through short pipes, called risers, covered by a cap with a serrated edge, or slots. The bubble-cap plate is the traditional, oldest, type of cross-flow plate, and many different designs have been developed. Standard cap designs would now be specified for most applications.

The most significant feature of the bubble-cap plate is that the use of risers ensures that a level of liquid is maintained on the tray at all vapour flow-rates.

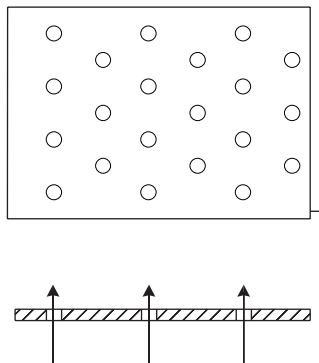


Figure 11.18. Sieve plate

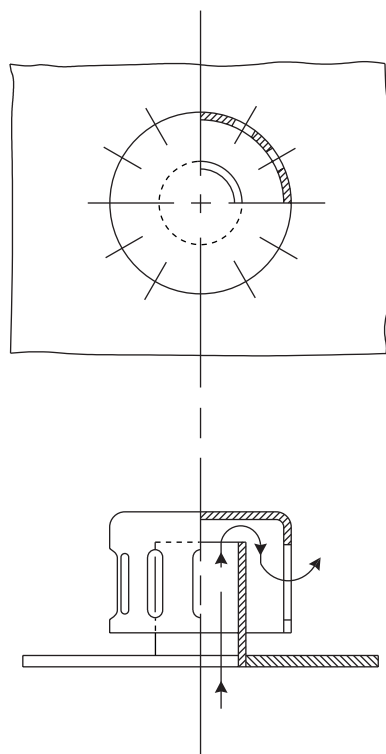


Figure 11.19. Bubble-cap

### 3. Valve plates (floating cap plates) (Figure 11.20)

Valve plates are proprietary designs. They are essentially sieve plates with large-diameter holes covered by movable flaps, which lift as the vapour flow increases.

As the area for vapour flow varies with the flow-rate, valve plates can operate efficiently at lower flow-rates than sieve plates: the valves closing at low vapour rates.



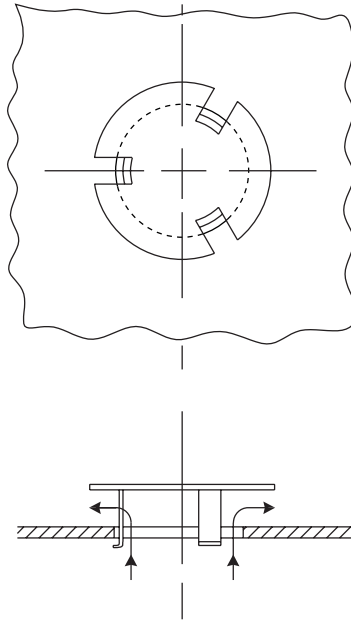


Figure 11.20. Simple valve

Some very elaborate valve designs have been developed, but the simple type shown in Figure 11.20 is satisfactory for most applications.

### ***Liquid flow pattern***

Cross-flow trays are also classified according to the number of liquid passes on the plate. The design shown in Figure 11.21a is a single-pass plate. For low liquid flow rates reverse flow plates are used; Figure 11.21b. In this type the plate is divided by a low central partition, and inlet and outlet downcomers are on the same side of the plate. Multiple-pass plates, in which the liquid stream is sub-divided by using several downcomers, are used for high liquid flow-rates and large diameter columns. A double-pass plate is shown in Figure 11.21c.

#### **11.12.1. Selection of plate type**

The principal factors to consider when comparing the performance of bubble-cap, sieve and valve plates are: cost, capacity, operating range, efficiency and pressure drop.

*Cost.* Bubble-cap plates are appreciably more expensive than sieve or valve plates. The relative cost will depend on the material of construction used; for mild steel the ratios, bubble-cap : valve : sieve, are approximately 3.0 : 1.5 : 1.0.

*Capacity.* There is little difference in the capacity rating of the three types (the diameter of the column required for a given flow-rate); the ranking is sieve, valve, bubble-cap.

*Operating range.* This is the most significant factor. By operating range is meant the range of vapour and liquid rates over which the plate will operate satisfactorily (the

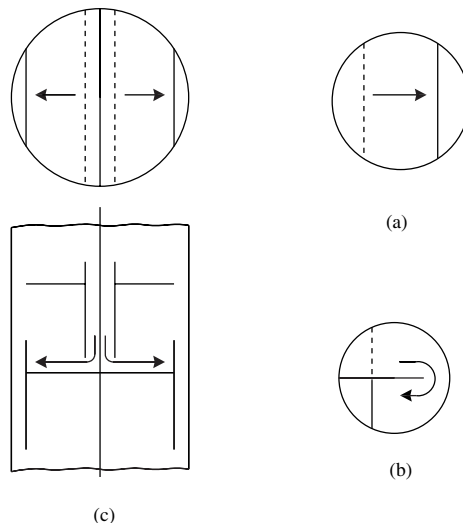


Figure 11.21. Liquid flow patterns on cross-flow trays. (a) Single pass (b) Reverse flow (c) Double pass

stable operating range). Some flexibility will always be required in an operating plant to allow for changes in production rate, and to cover start-up and shut-down conditions. The ratio of the highest to the lowest flow rates is often referred to as the “turn-down” ratio. Bubble-cap plates have a positive liquid seal and can therefore operate efficiently at very low vapour rates.

Sieve plates rely on the flow of vapour through the holes to hold the liquid on the plate, and cannot operate at very low vapour rates. But, with good design, sieve plates can be designed to give a satisfactory operating range; typically, from 50 per cent to 120 per cent of design capacity.

Valve plates are intended to give greater flexibility than sieve plates at a lower cost than bubble-caps.

*Efficiency.* The Murphree efficiency of the three types of plate will be virtually the same when operating over their design flow range, and no real distinction can be made between them; see Zuiderweg *et al.* (1960).

*Pressure drop.* The pressure drop over the plates can be an important design consideration, particularly for vacuum columns. The plate pressure drop will depend on the detailed design of the plate but, in general, sieve plates give the lowest pressure drop, followed by valves, with bubble-caps giving the highest.

*Summary.* Sieve plates are the cheapest and are satisfactory for most applications. Valve plates should be considered if the specified turn-down ratio cannot be met with sieve plates. Bubble-caps should only be used where very low vapour (gas) rates have to be handled and a positive liquid seal is essential at all flow-rates.

### 11.12.2. Plate construction

The mechanical design features of sieve plates are described in this section. The same general construction is also used for bubble-cap and valve plates. Details of the various

types of bubble-cap used, and the preferred dimensions of standard cap designs, can be found in the books by Smith (1963) and Ludwig (1997). The manufacturers' design manuals should be consulted for details of valve plate design; Glitsch (1970) and Koch (1960).

Two basically different types of plate construction are used. Large-diameter plates are normally constructed in sections, supported on beams. Small plates are installed in the column as a stack of pre-assembled plates.

### **Sectional construction**

A typical plate is shown in Figure 11.22. The plate sections are supported on a ring welded round the vessel wall, and on beams. The beams and ring are about 50 mm wide, with the beams set at around 0.6 m spacing. The beams are usually angle or channel sections, constructed from folded sheet. Special fasteners are used so the sections can be assembled from one side only. One section is designed to be removable to act as a manway. This reduces the number of manways needed on the vessel, which reduces the vessel cost.

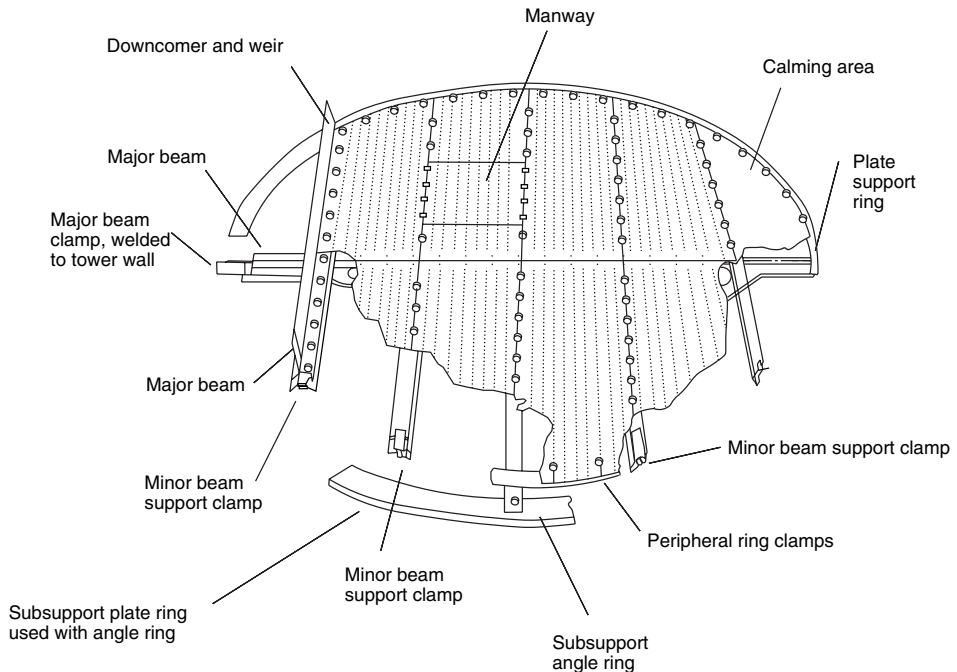


Figure 11.22. Typical sectional plate construction

Diagrams and photographs, of sectional plates, are given in Volume 2, Chapter 11.

### **Stacked plates (cartridge plates)**

The stacked type of construction is used where the column diameter is too small for a man to enter to assemble the plates, say less than 1.2 m (4 ft). Each plate is fabricated

complete with the downcomer, and joined to the plate above and below using screwed rods (spacers); see Figure 11.23. The plates are installed in the column shell as an assembly (stack) of ten, or so, plates. Tall columns have to be divided into flanged sections so that plate assemblies can be easily installed and removed. The weir, and downcomer supports, are usually formed by turning up the edge of the plate.

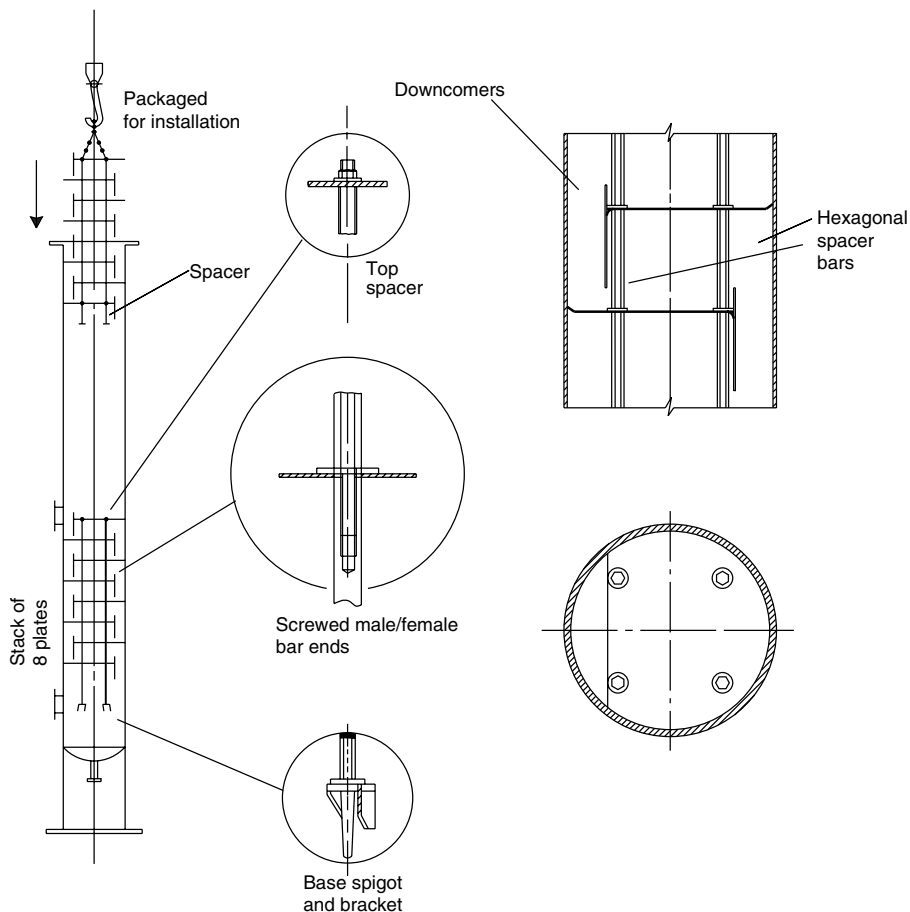


Figure 11.23. Typical stacked-plate construction

The plates are not fixed to the vessel wall, as they are with sectional plates, so there is no positive liquid seal at the edge of the plate, and a small amount of leakage will occur. In some designs the plate edges are turned up round the circumference to make better contact at the wall. This can make it difficult to remove the plates for cleaning and maintenance, without damage.

### **Downcomers**

The segmental, or chord downcomer, shown in Figure 11.24a is the simplest and cheapest form of construction and is satisfactory for most purposes. The downcomer channel is

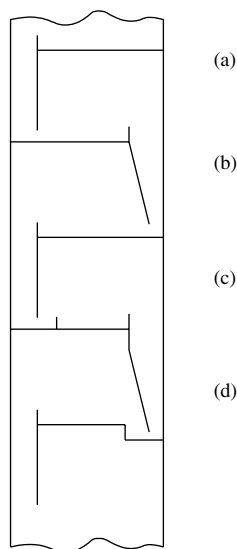


Figure 11.24. Segment (chord) downcomer designs. (a) Vertical apron (b) Inclined apron (c) Inlet weir (d) Recessed well

formed by a flat plate, called an apron, which extends down from the outlet weir. The apron is usually vertical, but may be sloped (Figure 11.24*b*) to increase the plate area available for perforation. If a more positive seal is required at the downcomer at the outlet, an inlet weir can be fitted (Figure 11.24*c*) or a recessed seal pan used (Figure 11.24*d*). Circular downcomers (pipes) are sometimes used for small liquid flow-rates.

### ***Side-stream and feed points***

Where a side-stream is withdrawn from the column the plate design must be modified to provide a liquid seal at the take-off pipe. A typical design is shown in Figure 11.25*a*. When the feed stream is liquid it will be normally introduced into the downcomer leading to the feed plate, and the plate spacing increased at this point; Figure 11.25*b*.

### ***Structural design***

The plate structure must be designed to support the hydraulic loads on the plate during operation, and the loads imposed during construction and maintenance. Typical design values used for these loads are:

Hydraulic load:  $600 \text{ N/m}^2$  live load on the plate, plus  $3000 \text{ N/m}^2$  over the downcomer seal area.

Erection and maintenance:  $1500 \text{ N}$  concentrated load on any structural member.

It is important to set close tolerances on the weir height, downcomer clearance, and plate flatness, to ensure an even flow of liquid across the plate. The tolerances specified will depend on the dimensions of the plate but will typically be about  $3 \text{ mm}$ .

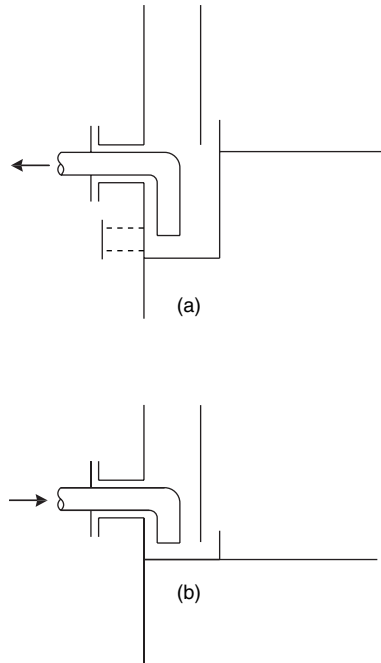


Figure 11.25. Feed and take-off nozzles

The plate deflection under load is also important, and will normally be specified as not greater than 3 mm under the operating conditions for plates greater than 2.5 m, and proportionally less for smaller diameters.

The mechanical specification of bubble-cap, sieve and valve plates is covered in a series of articles by Glitsch (1960), McClain (1960), Thrift (1960*a, b*) and Patton and Pritchard (1960).

### 11.13. PLATE HYDRAULIC DESIGN

The basic requirements of a plate contacting stage are that it should:

- Provide good vapour-liquid contact.
- Provide sufficient liquid hold-up for good mass transfer (high efficiency).
- Have sufficient area and spacing to keep the entrainment and pressure drop within acceptable limits.
- Have sufficient downcomer area for the liquid to flow freely from plate to plate.

Plate design, like most engineering design, is a combination theory and practice. The design methods use semi-empirical correlations derived from fundamental research work combined with practical experience obtained from the operation of commercial columns. Proven layouts are used, and the plate dimensions are kept within the range of values known to give satisfactory performance.

A short procedure for the hydraulic design of sieve plates is given in this section. Design methods for bubble-cap plates are given by Bolles (1963) and Ludwig (1997). Valve plates are proprietary designs and will be designed in consultation with the vendors. Design manuals are available from some vendors; Glistch (1970) and Koch (1960).

A detailed discussion of the extensive literature on plate design and performance will not be given in this volume. Chase (1967) and Zuiderweg (1982) give critical reviews of the literature on sieve plates.

Several design methods have been published for sieve plates: Kister (1992), Barnicki and Davies (1989), Koch and Kuzniar (1966), Fair (1963), and Huang and Hodson (1958); see also the book by Lockett (1986).

### **Operating range**

Satisfactory operation will only be achieved over a limited range of vapour and liquid flow rates. A typical performance diagram for a sieve plate is shown in Figure 11.26.

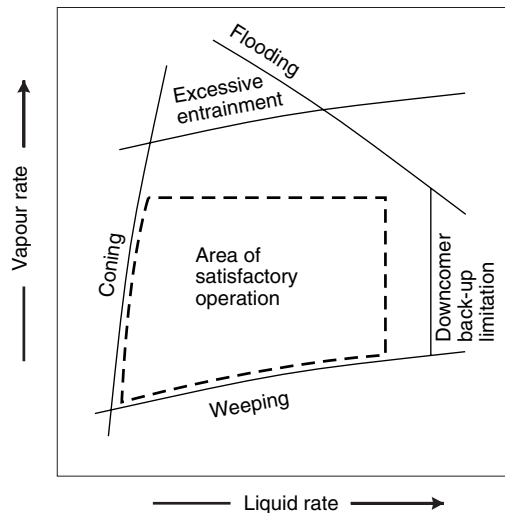


Figure 11.26. Sieve plate performance diagram

The upper limit to vapour flow is set by the condition of flooding. At flooding there is a sharp drop in plate efficiency and increase in pressure drop. Flooding is caused by either the excessive carry over of liquid to the next plate by entrainment, or by liquid backing-up in the downcomers.

The lower limit of the vapour flow is set by the condition of weeping. Weeping occurs when the vapour flow is insufficient to maintain a level of liquid on the plate. "Coning" occurs at low liquid rates, and is the term given to the condition where the vapour pushes the liquid back from the holes and jets upward, with poor liquid contact.

In the following sections gas can be taken as synonymous with vapour when applying the method to the design of plates for absorption columns.

### 11.13.1. Plate-design procedure

A trial-and-error approach is necessary in plate design: starting with a rough plate layout, checking key performance factors and revising the design, as necessary, until a satisfactory design is achieved. A typical design procedure is set out below and discussed in the following sections. The normal range of each design variable is given in the discussion, together with recommended values which can be used to start the design.

#### **Procedure**

1. Calculate the maximum and minimum vapour and liquid flow-rates, for the turn down ratio required.
2. Collect, or estimate, the system physical properties.
3. Select a trial plate spacing (Section 11.11).
4. Estimate the column diameter, based on flooding considerations (Section 11.13.3).
5. Decide the liquid flow arrangement (Section 11.13.4).
6. Make a trial plate layout: downcomer area, active area, hole area, hole size, weir height (Sections 11.13.8 to 11.13.10).
7. Check the weeping rate (Section 11.13.6), if unsatisfactory return to step 6.
8. Check the plate pressure drop (Section 11.13.14), if too high return to step 6.
9. Check downcomer back-up, if too high return to step 6 or 3 (Section 11.13.15).
10. Decide plate layout details: calming zones, unperforated areas. Check hole pitch, if unsatisfactory return to step 6 (Section 11.13.11).
11. Recalculate the percentage flooding based on chosen column diameter.
12. Check entrainment, if too high return to step 4 (Section 11.13.5).
13. Optimise design: repeat steps 3 to 12 to find smallest diameter and plate spacing acceptable (lowest cost).
14. Finalise design: draw up the plate specification and sketch the layout.

This procedure is illustrated in Example 11.11.

### 11.13.2. Plate areas

The following areas terms are used in the plate design procedure:

- $A_c$  = total column cross-sectional area,
- $A_d$  = cross-sectional area of downcomer,
- $A_n$  = net area available for vapour-liquid disengagement, normally equal to  $A_c - A_d$ ,  
for a single pass plate,
- $A_a$  = active, or bubbling, area, equal to  $A_c - 2A_d$  for single-pass plates,
- $A_h$  = hole area, the total area of all the active holes,
- $A_p$  = perforated area (including blanked areas),
- $A_{ap}$  = the clearance area under the downcomer apron.

### 11.13.3. Diameter

The flooding condition fixes the upper limit of vapour velocity. A high vapour velocity is needed for high plate efficiencies, and the velocity will normally be between 70 to



90 per cent of that which would cause flooding. For design, a value of 80 to 85 per cent of the flooding velocity should be used.

The flooding velocity can be estimated from the correlation given by Fair (1961):

$$u_f = K_1 \sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \quad (11.81)$$

where  $u_f$  = flooding vapour velocity, m/s, based on the net column cross-sectional area  $A_n$  (see Section 11.13.2),

$K_1$  = a constant obtained from Figure 11.27.

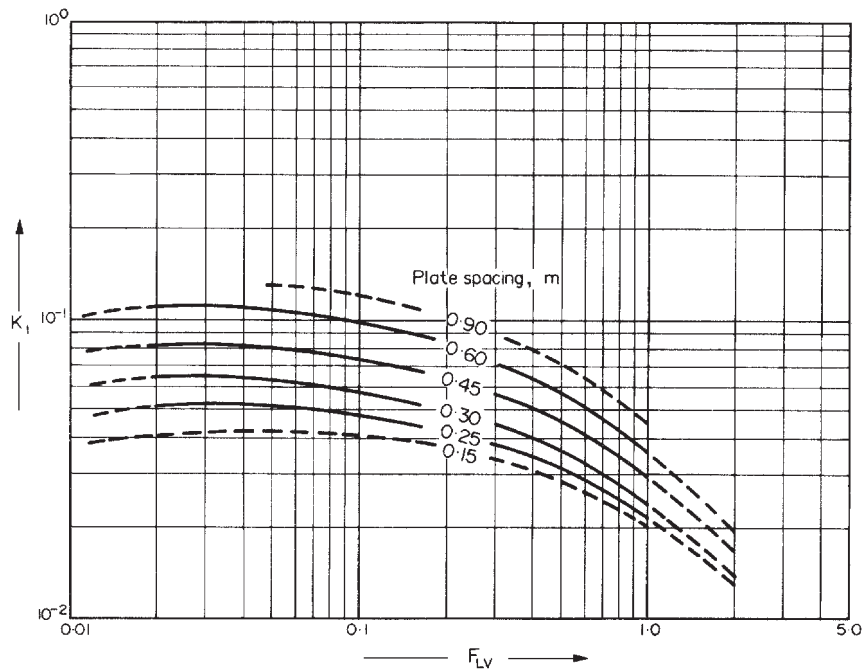


Figure 11.27. Flooding velocity, sieve plates

The liquid-vapour flow factor  $F_{LV}$  in Figure 11.27 is given by:

$$F_{LV} = \frac{L_w}{V_w} \sqrt{\frac{\rho_v}{\rho_L}} \quad (11.82)$$

where  $L_w$  = liquid mass flow-rate, kg/s,

$V_w$  = vapour mass flow-rate, kg/s.

The following restrictions apply to the use of Figure 11.27:

1. Hole size less than 6.5 mm. Entrainment may be greater with larger hole sizes.
2. Weir height less than 15 per cent of the plate spacing.

3. Non-foaming systems.
4. Hole: active area ratio greater than 0.10; for other ratios apply the following corrections:

hole: active area	multiply $K_1$ by
0.10	1.0
0.08	0.9
0.06	0.8

5. Liquid surface tension 0.02 N/m, for other surface tensions  $\sigma$  multiply the value of  $K_1$  by  $[\sigma/0.02]^{0.2}$ .

To calculate the column diameter an estimate of the net area  $A_n$  is required. As a first trial take the downcomer area as 12 per cent of the total, and assume that the hole-active area is 10 per cent.

Where the vapour and liquid flow-rates, or physical properties, vary significantly throughout the column a plate design should be made for several points up the column. For distillation it will usually be sufficient to design for the conditions above and below the feed points. Changes in the vapour flow-rate will normally be accommodated by adjusting the hole area; often by blanking off some rows of holes. Different column diameters would only be used where there is a considerable change in flow-rate. Changes in liquid rate can be allowed for by adjusting the liquid downcomer areas.

#### 11.13.4. Liquid-flow arrangement

The choice of plate type (reverse, single pass or multiple pass) will depend on the liquid flow-rate and column diameter. An initial selection can be made using Figure 11.28, which has been adapted from a similar figure given by Huang and Hodson (1958).

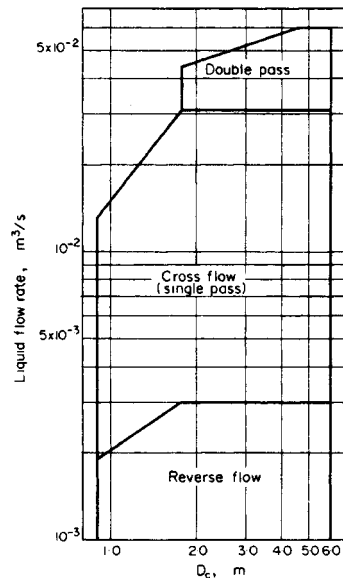


Figure 11.28. Selection of liquid-flow arrangement

### 11.13.5. Entrainment

Entrainment can be estimated from the correlation given by Fair (1961), Figure 11.29, which gives the fractional entrainment  $\psi$  (kg/kg gross liquid flow) as a function of the liquid-vapour factor  $F_{LV}$ , with the percentage approach to flooding as a parameter.

The percentage flooding is given by:

$$\text{percentage flooding} = \frac{u_n \text{ actual velocity (based on net area)}}{u_f \text{ (from equation 11.81)}} \quad (11.83)$$

The effect of entrainment on plate efficiency can be estimated using equation 11.78.

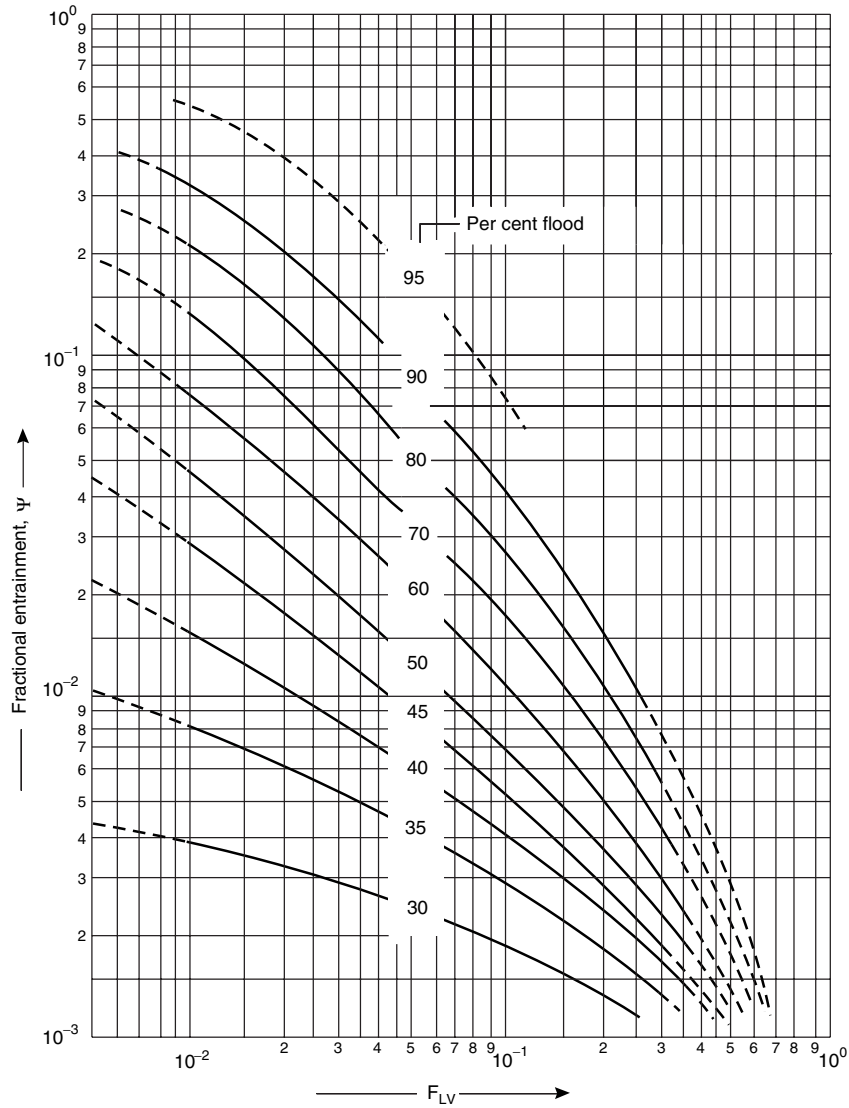


Figure 11.29. Entrainment correlation for sieve plates (Fair, 1961)

As a rough guide the upper limit of  $\psi$  can be taken as 0.1; below this figure the effect on efficiency will be small. The optimum design value may be above this figure, see Fair (1963).

### 11.13.6. Weep point

The lower limit of the operating range occurs when liquid leakage through the plate holes becomes excessive. This is known as the weep point. The vapour velocity at the weep point is the minimum value for stable operation. The hole area must be chosen so that at the lowest operating rate the vapour flow velocity is still well above the weep point.

Several correlations have been proposed for predicting the vapour velocity at the weep point; see Chase (1967). That given by Eduljee (1959) is one of the simplest to use, and has been shown to be reliable.

The minimum design vapour velocity is given by:

$$\check{u}_h = \frac{[K_2 - 0.90(25.4 - d_h)]}{(\rho_v)^{1/2}} \quad (11.84)$$

where  $\check{u}_h$  = minimum vapour velocity through the holes(based on the hole area), m/s,

$d_h$  = hole diameter, mm,

$K_2$  = a constant, dependent on the depth of clear liquid on the plate, obtained from Figure 11.30.

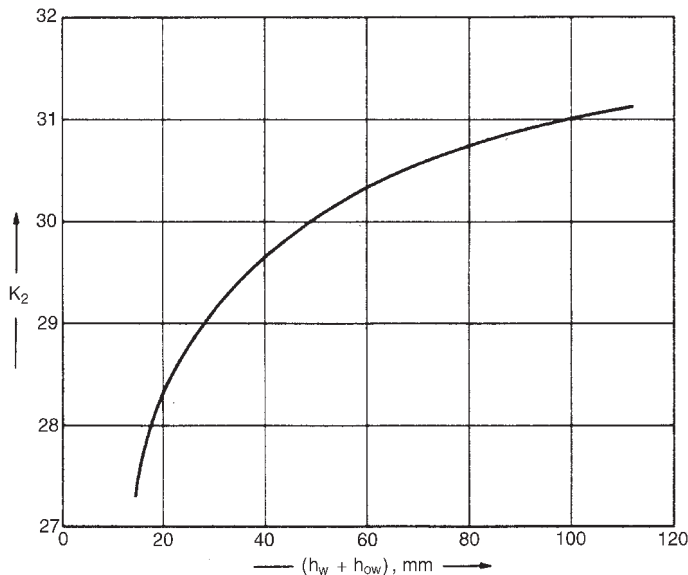


Figure 11.30. Weep-point correlation (Eduljee, 1959)

The clear liquid depth is equal to the height of the weir  $h_w$  plus the depth of the crest of liquid over the weir  $h_{ow}$ ; this is discussed in the next section.

### 11.13.7. Weir liquid crest

The height of the liquid crest over the weir can be estimated using the Francis weir formula (see Volume 1, Chapter 5). For a segmental downcomer this can be written as:

$$h_{ow} = 750 \left[ \frac{L_w}{\rho_L l_w} \right]^{2/3} \quad (11.85)$$

where  $l_w$  = weir length, m,

$h_{ow}$  = weir crest, mm liquid,

$L_w$  = liquid flow-rate, kg/s.

With segmental downcomers the column wall constricts the liquid flow, and the weir crest will be higher than that predicted by the Francis formula for flow over an open weir. The constant in equation 11.85 has been increased to allow for this effect.

To ensure an even flow of liquid along the weir, the crest should be at least 10 mm at the lowest liquid rate. Serrated weirs are sometimes used for very low liquid rates.

### 11.13.8. Weir dimensions

#### **Weir height**

The height of the weir determines the volume of liquid on the plate and is an important factor in determining the plate efficiency (see Section 11.10.4). A high weir will increase the plate efficiency but at the expense of a higher plate pressure drop. For columns operating above atmospheric pressure the weir heights will normally be between 40 mm to 90 mm (1.5 to 3.5 in.); 40 to 50 mm is recommended. For vacuum operation lower weir heights are used to reduce the pressure drop; 6 to 12 mm ( $\frac{1}{4}$  to  $\frac{1}{2}$  in.) is recommended.

#### **Inlet weirs**

Inlet weirs, or recessed pans, are sometimes used to improve the distribution of liquid across the plate; but are seldom needed with segmental downcomers.

#### **Weir length**

With segmental downcomers the length of the weir fixes the area of the downcomer. The chord length will normally be between 0.6 to 0.85 of the column diameter. A good initial value to use is 0.77, equivalent to a downcomer area of 12 per cent.

The relationship between weir length and downcomer area is given in Figure 11.31.

For double-pass plates the width of the central downcomer is normally 200–250 mm (8–10 in.).

### 11.13.9. Perforated area

The area available for perforation will be reduced by the obstruction caused by structural members (the support rings and beams), and by the use of calming zones.

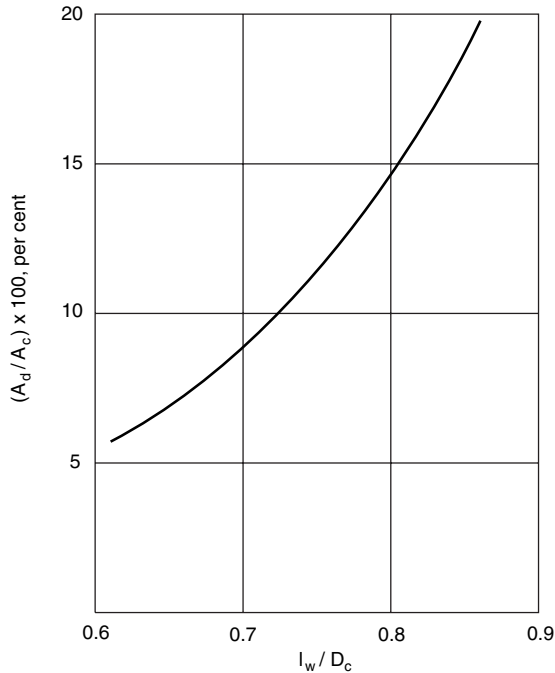


Figure 11.31. Relation between downcomer area and weir length

Calming zones are unperforated strips of plate at the inlet and outlet sides of the plate. The width of each zone is usually made the same; recommended values are: below 1.5 m diameter, 75 mm; above, 100 mm.

The width of the support ring for sectional plates will normally be 50 to 75 mm: the support ring should not extend into the downcomer area. A strip of unperforated plate will be left round the edge of cartridge-type trays to stiffen the plate.

The unperforated area can be calculated from the plate geometry. The relationship between the weir chord length, chord height and the angle subtended by the chord is given in Figure 11.32.

#### 11.13.10. Hole size

The hole sizes used vary from 2.5 to 12 mm; 5 mm is the preferred size. Larger holes are occasionally used for fouling systems. The holes are drilled or punched. Punching is cheaper, but the minimum size of hole that can be punched will depend on the plate thickness. For carbon steel, hole sizes approximately equal to the plate thickness can be punched, but for stainless steel the minimum hole size that can be punched is about twice the plate thickness. Typical plate thicknesses used are: 5 mm (3/16 in.) for carbon steel, and 3 mm (12 gauge) for stainless steel.

When punched plates are used they should be installed with the direction of punching upward. Punching forms a slight nozzle, and reversing the plate will increase the pressure drop.

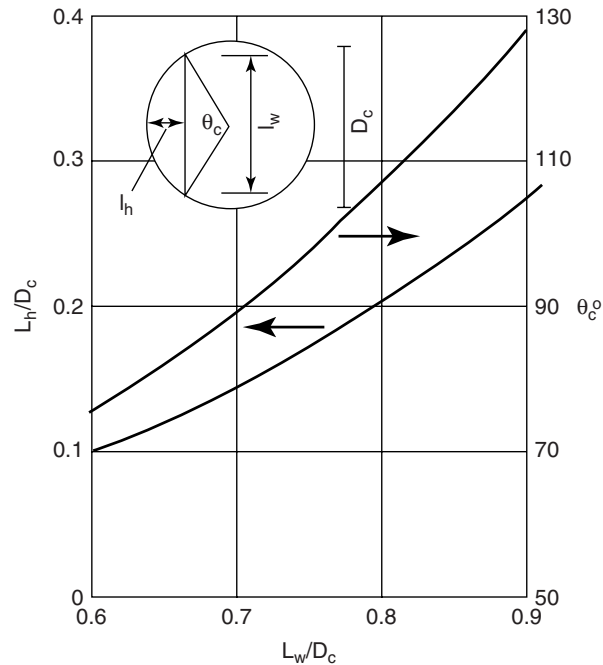


Figure 11.32. Relation between angle subtended by chord, chord height and chord length

### 11.13.11. Hole pitch

The hole pitch (distance between the hole centres)  $l_p$  should not be less than 2.0 hole diameters, and the normal range will be 2.5 to 4.0 diameters. Within this range the pitch can be selected to give the number of active holes required for the total hole area specified.

Square and equilateral triangular patterns are used; triangular is preferred. The total hole area as a fraction of the perforated area  $A_p$  is given by the following expression, for an equilateral triangular pitch:

$$\frac{A_h}{A_p} = 0.9 \left[ \frac{d_h}{l_p} \right]^2 \quad (11.86)$$

This equation is plotted in Figure 11.33.

### 11.13.12. Hydraulic gradient

The hydraulic gradient is the difference in liquid level needed to drive the liquid flow across the plate. On sieve plates, unlike bubble-cap plates, the resistance to liquid flow will be small, and the hydraulic gradient is usually ignored in sieve-plate design. It can be significant in vacuum operation, as with the low weir heights used the hydraulic gradient can be a significant fraction of the total liquid depth. Methods for estimating the hydraulic gradient are given by Fair (1963).

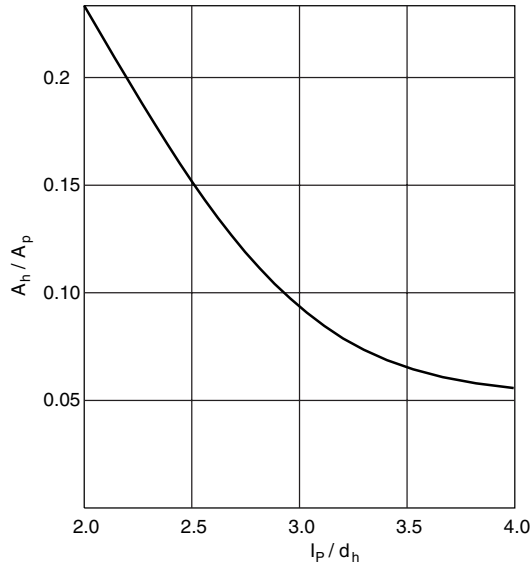


Figure 11.33. Relation between hole area and pitch

### 11.13.13. Liquid throw

The liquid throw is the horizontal distance travelled by the liquid stream flowing over the downcomer weir. It is only an important consideration in the design of multiple-pass plates. Bolles (1963) gives a method for estimating the liquid throw.

### 11.13.14. Plate pressure drop

The pressure drop over the plates is an important design consideration. There are two main sources of pressure loss: that due to vapour flow through the holes (an orifice loss), and that due to the static head of liquid on the plate.

A simple additive model is normally used to predict the total pressure drop. The total is taken as the sum of the pressure drop calculated for the flow of vapour through the dry plate (the dry plate drop  $h_d$ ); the head of clear liquid on the plate ( $h_w + h_{ow}$ ); and a term to account for other, minor, sources of pressure loss, the so-called residual loss  $h_r$ . The residual loss is the difference between the observed experimental pressure drop and the simple sum of the dry-plate drop and the clear-liquid height. It accounts for the two effects: the energy to form the vapour bubbles and the fact that on an operating plate the liquid head will not be clear liquid but a head of “aerated” liquid froth, and the froth density and height will be different from that of the clear liquid.

It is convenient to express the pressure drops in terms of millimetres of liquid. In pressure units:

$$\Delta P_t = 9.81 \times 10^{-3} h_t \rho_L \quad (11.87)$$

where  $\Delta P_t$  = total plate pressure drop, Pa(N/m<sup>2</sup>),

$h_t$  = total plate pressure drop, mm liquid.



### Dry plate drop

The pressure drop through the dry plate can be estimated using expressions derived for flow through orifices.

$$h_d = 51 \left[ \frac{u_h}{C_0} \right]^2 \frac{\rho_v}{\rho_L} \quad (11.88)$$

where the orifice coefficient  $C_0$  is a function of the plate thickness, hole diameter, and the hole to perforated area ratio.  $C_0$  can be obtained from Figure 11.34; which has been adapted from a similar figure by Liebson *et al.* (1957).  $u_h$  is the velocity through the holes, m/s.

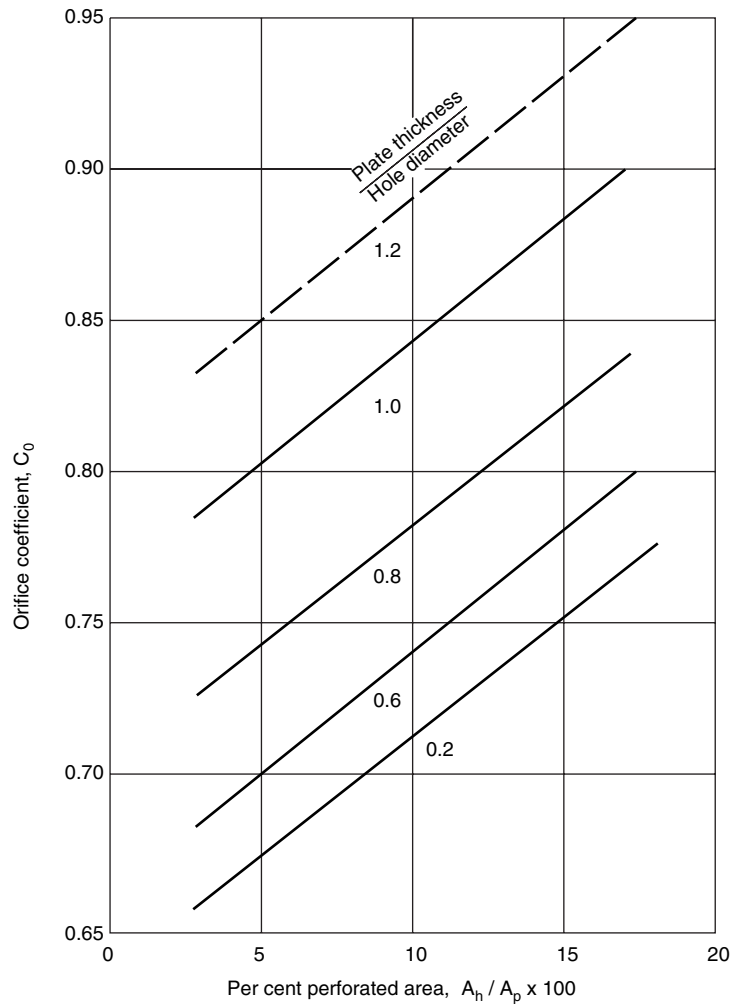


Figure 11.34. Discharge coefficient, sieve plates (Liebson *et al.*, 1957)

### Residual head

Methods have been proposed for estimating the residual head as a function of liquid surface tension, froth density and froth height. However, as this correction term is small the use of an elaborate method for its estimation is not justified, and the simple equation proposed by Hunt *et al.* (1955) can be used:

$$h_r = \frac{12.5 \times 10^3}{\rho_L} \quad (11.89)$$

Equation 11.89 is equivalent to taking the residual drop as a fixed value of 12.5 mm of water ( $\frac{1}{2}$  in.).

### Total drop

The total plate drop is given by:

$$h_t = h_d + (h_w + h_{ow}) + h_r \quad (11.90)$$

If the hydraulic gradient is significant, half its value is added to the clear liquid height.

#### 11.13.15. Downcomer design [back-up]

The downcomer area and plate spacing must be such that the level of the liquid and froth in the downcomer is well below the top of the outlet weir on the plate above. If the level rises above the outlet weir the column will flood.

The back-up of liquid in the downcomer is caused by the pressure drop over the plate (the downcomer in effect forms one leg of a U-tube) and the resistance to flow in the downcomer itself; see Figure 11.35.

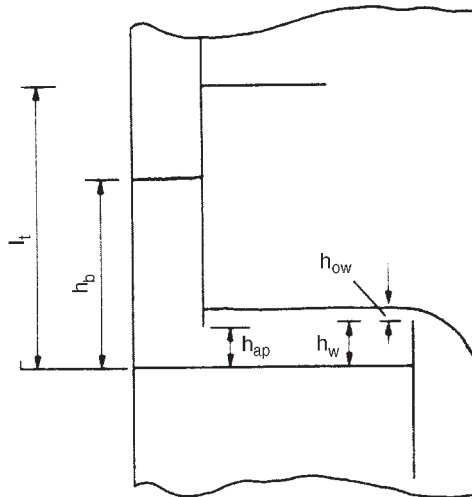


Figure 11.35. Downcomer back-up

In terms of clear liquid the downcomer back-up is given by:

$$h_b = (h_w + h_{ow}) + h_t + h_{dc} \quad (11.91)$$

where  $h_b$  = downcomer back-up, measured from plate surface, mm,

$h_{dc}$  = head loss in the downcomer, mm.

The main resistance to flow will be caused by the constriction at the downcomer outlet, and the head loss in the downcomer can be estimated using the equation given by Cicalese *et al.* (1947)

$$h_{dc} = 166 \left[ \frac{L_{wd}}{\rho_L A_m} \right]^2 \quad (11.92)$$

where  $L_{wd}$  = liquid flow rate in downcomer, kg/s,

$A_m$  = either the downcomer area  $A_d$  or the clearance area under the downcomer  $A_{ap}$ ; whichever is the smaller,  $m^2$ .

The clearance area under the downcomer is given by:

$$A_{ap} = h_{ap} l_w \quad (11.93)$$

where  $h_{ap}$  is height of the bottom edge of the apron above the plate. This height is normally set at 5 to 10 mm ( $\frac{1}{4}$  to  $\frac{1}{2}$  in.) below the outlet weir height:

$$h_{ap} = h_w - (5 \text{ to } 10 \text{ mm})$$

### **Froth height**

To predict the height of “aerated” liquid on the plate, and the height of froth in the downcomer, some means of estimating the froth density is required. The density of the “aerated” liquid will normally be between 0.4 to 0.7 times that of the clear liquid. A number of correlations have been proposed for estimating froth density as a function of the vapour flow-rate and the liquid physical properties; see Chase (1967); however, none is particularly reliable, and for design purposes it is usually satisfactory to assume an average value of 0.5 of the liquid density.

This value is also taken as the mean density of the fluid in the downcomer; which means that for safe design the clear liquid back-up, calculated from equation 11.91, should not exceed half the plate spacing  $l_t$ , to avoid flooding.

Allowing for the weir height:

$$h_b \not\leq \frac{1}{2}(l_t + h_w) \quad (11.94)$$

This criterion is, if anything, oversafe, and where close plate spacing is desired a better estimate of the froth density in the downcomer should be made. The method proposed by Thomas and Shah (1964) is recommended.

### **Downcomer residence time**

Sufficient residence time must be allowed in the downcomer for the entrained vapour to disengage from the liquid stream; to prevent heavily “aerated” liquid being carried under the downcomer.

A time of at least 3 seconds is recommended.

The downcomer residence time is given by:

$$t_r = \frac{A_d h_{bc} \rho_L}{L_{wd}} \quad (11.95)$$

where  $t_r$  = residence time, s,

$h_{bc}$  = clear liquid back-up, m.

### Example 11.11

Design the plates for the column specified in Example 11.2. Take the minimum feed rate as 70 per cent of the maximum (maximum feed 10,000 kg/h). Use sieve plates.

### Solution

As the liquid and vapour flow-rates and compositions will vary up the column, plate designs should be made above and below the feed point. Only the bottom plate will be designed in detail in this example.

From McCabe-Thiele diagram, Example 11.2:

Number of stages = 16

Slope of the bottom operating line = 5.0

Slope of top operating line = 0.57

Top composition 94 per cent mol. 98 per cent w/w.

Bottom composition — essentially water.

Reflux ratio = 1.35

### Flow-rates

Mol. weight feed =  $0.033 \times 58 + (1 - 0.033)18 = 19.32$

Feed =  $13,000/19.32 = 672.9$  kmol/h

A mass balance on acetone gives:

Top product,  $D = 672.9 \times 0.033/0.94 = 23.6$  kmol/h

Vapour rate,  $V = D(1 + R) = 23.6(1 + 1.35) = 55.5$  kmol/h

An overall mass balance gives:

Bottom product,  $B = 672.9 - 23.6 = 649.3$  kmol/h

Slope of the bottom operating line  $L_m'/V_m' = 5.0$

and  $V_m' = L_m' - B$ , from which:

vapour flow below feed,  $V_m' = 162.3$  kmol/h

liquid flow below feed,  $L_m' = 811.6$  kmol/h

### Physical properties

Estimate base pressure, assume column efficiency of 60 per cent, take reboiler as equivalent to one stage.

$$\text{Number of real stages} = \frac{16 - 1}{0.6} = 25$$

Assume 100 mm water, pressure drop per plate.

$$\text{Column pressure drop} = 100 \times 10^{-3} \times 1000 \times 9.81 \times 25 = 24,525 \text{ Pa}$$

$$\text{Top pressure, 1 atm (14.7 lb/in}^2\text{)} = 101.4 \times 10^3 \text{ Pa}$$

$$\begin{aligned} \text{Estimated bottom pressure} &= 101.4 \times 10^3 + 24,525 \\ &= 125,925 \text{ Pa} = \underline{\underline{1.26 \text{ bar}}} \end{aligned}$$

From steam tables, base temperature 106°C.

$$\rho_v = 0.72 \text{ kg/m}^3$$

$$\rho_L = 954 \text{ kg/m}^3$$

$$\text{Surface tension } 57 \times 10^{-3} \text{ N/m}$$

Top, 98% w/w acetone, top temperature 57°C

From PPDS (see Chapter 8);

$$\rho_v = 2.05 \text{ kg/m}^3, \rho_L = 753 \text{ kg/m}^3$$

$$\text{Molecular weight } 55.6$$

$$\text{Surface tension } 23 \times 10^{-3} \text{ N/m}$$

### **Column diameter**

$$F_{LV} \text{ bottom} = 5.0 \sqrt{\frac{0.72}{954}} = 0.14 \quad (11.82)$$

$$F_{LV} \text{ top} = 0.57 \sqrt{\frac{2.05}{753}} = 0.03$$

Take plate spacing as 0.5 m

From Figure 11.27

$$\text{base } K_1 = 7.5 \times 10^{-2}$$

$$\text{top } K_1 = 9.0 \times 10^{-2}$$

Correction for surface tensions

$$\text{base } K_1 = \left(\frac{57}{20}\right)^{0.2} \times 7.5 \times 10^{-2} = 9.3 \times 10^{-2}$$

$$\text{top } K_1 = \left(\frac{23}{20}\right)^{0.2} \times 9.0 \times 10^{-2} = 9.3 \times 10^{-2}$$

$$\text{base } u_f = 9.3 \times 10^{-2} \sqrt{\frac{954 - 0.72}{0.72}} = 3.38 \text{ m/s} \quad (11.81)$$

$$\text{top } u_f = 9.3 \times 10^{-2} \sqrt{\frac{753 - 2.05}{2.05}} = 1.78 \text{ m/s}$$

Design for 85 per cent flooding at maximum flow rate

$$\text{base } \hat{u}_v = 3.38 \times 0.85 = 2.87 \text{ m/s}$$

$$\text{top } \hat{u}_v = 1.78 \times 0.85 = 1.51 \text{ m/s}$$

Maximum volumetric flow-rate

$$\text{base} = \frac{162.3 \times 18}{0.72 \times 3600} = 1.13 \text{ m}^3/\text{s}$$

$$\text{top} = \frac{55.5 \times 55.6}{2.05 \times 3600} = 0.42 \text{ m}^3/\text{s}$$

Net area required

$$\text{bottom} = \frac{1.13}{2.87} = 0.40 \text{ m}^2$$

$$\text{top} = \frac{0.42}{1.51} = 0.28 \text{ m}^2$$

As first trial take downcomer area as 12 per cent of total.

Column cross-sectioned area

$$\text{base} = \frac{0.40}{0.88} = 0.46 \text{ m}^2$$

$$\text{top} = \frac{0.28}{0.88} = 0.32 \text{ m}^2$$

Column diameter

$$\text{base} = \sqrt{\frac{0.46 \times 4}{\pi}} = 0.77 \text{ m}$$

$$\text{top} = \sqrt{\frac{0.34 \times 4}{\pi}} = 0.64 \text{ m}$$

Use same diameter above and below feed, reducing the perforated area for plates above the feed.

Nearest standard pipe size (BS 1600); outside diameter 812.8 mm (32 in); standard wall thickness 9.52 mm; inside diameter 794 mm.

### **Liquid flow pattern**

$$\text{Maximum volumetric liquid rate} = \frac{811.6 \times 18}{3600 \times 954} = 4.3 \times 10^{-3} \text{ m}^3/\text{s}$$

The plate diameter is outside the range of Figure 11.28, but it is clear that a single pass plate can be used.

### **Provisional plate design**

Column diameter  $D_c = 0.79 \text{ m}$

Column area  $A_c = 0.50 \text{ m}^2$

Downcomer area  $A_d = 0.12 \times 0.50 = 0.06 \text{ m}^2$ , at 12 per cent

Net area  $A_n = A_c - A_d = 0.50 - 0.06 = 0.44 \text{ m}^2$

$$\text{Active area } A_a = A_c - 2A_d = 0.50 - 0.12 = 0.38 \text{ m}^2$$

$$\text{Hole area } A_h \text{ take 10 per cent } A_a \text{ as first trial} = 0.038 \text{ m}^2$$

$$\text{Weir length (from Figure 11.31)} = 0.76 \times 0.79 = 0.60 \text{ m}$$

Take weir height	50 mm
Hole diameter	5 mm
Plate thickness	5 mm

### ***Check weeping***

$$\text{Maximum liquid rate} = \left( \frac{811.6 \times 18}{3600} \right) = 4.06 \text{ kg/s}$$

$$\text{Minimum liquid rate, at 70 per cent turn-down} = 0.7 \times 4.06 = 2.84 \text{ kg/s}$$

$$\text{maximum } h_{ow} = 750 \left( \frac{4.06}{954 \times 0.06} \right)^{2/3} = 27 \text{ mm liquid} \quad (11.85)$$

$$\text{minimum } h_{ow} = 750 \left( \frac{2.85}{954 \times 0.60} \right)^{2/3} = 22 \text{ mm liquid}$$

$$\text{at minimum rate } h_w + h_{ow} = 50 + 22 = 72 \text{ mm}$$

$$\text{From Figure 11.30, } K_2 = 30.6$$

$$\check{u}_h(\text{min}) = \frac{30.6 - 0.90(25.4 - 5)}{(0.72)^{1/2}} = 14 \text{ m/s} \quad (11.84)$$

$$\begin{aligned} \text{actual minimum vapour velocity} &= \frac{\text{minimum vapour rate}}{A_h} \\ &= \frac{0.7 \times 1.13}{0.038} = 20.8 \text{ m/s} \end{aligned}$$

So minimum operating rate will be well above weep point.

### ***Plate pressure drop***

Dry plate drop

Maximum vapour velocity through holes

$$\hat{u}_h = \frac{1.13}{0.038} = 29.7 \text{ m/s}$$

From Figure 11.34, for plate thickness/hole dia. = 1, and  $A_h/A_p \simeq A_h/A_a = 0.1$ ,  $C_0 = 0.84$

$$h_d = 51 \left( \frac{29.7}{0.84} \right)^2 \frac{0.72}{954} = 48 \text{ mm liquid} \quad (11.88)$$

residual head

$$h_r = \frac{12.5 \times 10^3}{954} = 13.1 \text{ mm liquid} \quad (11.89)$$

total plate pressure drop

$$h_t = 48 + (50 + 27) + 13 = 138 \text{ mm liquid}$$

*Note:* 100 mm was assumed to calculate the base pressure. The calculation could be repeated with a revised estimate but the small change in physical properties will have little effect on the plate design. 138 mm per plate is considered acceptable.

### **Downcomer liquid back-up**

Downcomer pressure loss

Take  $h_{ap} = h_w - 10 = 40$  mm.

Area under apron,  $A_{ap} = 0.60 \times 40 \times 10^{-3} = 0.024$  m<sup>2</sup>.

As this is less than  $A_d = 0.06$  m<sup>2</sup> use  $A_{ap}$  in equation 11.92

$$h_{dc} = 166 \left( \frac{4.06}{954 \times 0.024} \right)^2 = 5.2 \text{ mm} \quad (11.92)$$

say 6 mm.

Back-up in downcomer

$$h_b = (50 + 27) + 138 + 6 = 221 \text{ mm} \quad (11.91)$$

0.22 m

$0.22 < \frac{1}{2}(\text{plate spacing} + \text{weir height})$   
so plate spacing is acceptable

Check residence time

$$t_r = \frac{0.06 \times 0.22 \times 954}{4.06} = 3.1 \text{ s} \quad (11.95)$$

$> 3$  s, satisfactory.

### **Check entrainment**

$$u_v = \frac{1.13}{0.44} = 2.57 \text{ m/s}$$

per cent flooding =  $\frac{2.57}{3.38} = 76$

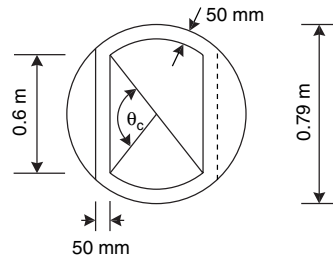
$F_{LV} = \underline{0.14}$ , from Figure 11.29,  $\Psi = 0.018$ , well below 0.1.

As the per cent flooding is well below the design figure of 85, the column diameter could be reduced, but this would increase the pressure drop.

### **Trial layout**

Use cartridge-type construction. Allow 50 mm unperforated strip round plate edge; 50 mm wide calming zones.





### Perforated area

From Figure 11.32, at  $l_w/D_c = 0.6/0.79 = 0.76$   
 $\theta_c = 99^\circ$

angle subtended by the edge of the plate =  $180 - 99 = 81^\circ$

mean length, unperforated edge strips =  $(0.79 - 50 \times 10^{-3})\pi \times 81/180 = 1.05$  m

area of unperforated edge strips =  $50 \times 10^{-3} \times 1.05 = 0.053$  m<sup>2</sup>

mean length of calming zone, approx. = weir length + width of unperforated strip  
 $= 0.6 + 50 \times 10^{-3} = 0.65$  m

area of calming zones =  $2(0.65 \times 50 \times 10^{-3}) = 0.065$  m<sup>2</sup>

total area for perforations,  $A_p = 0.38 - 0.053 - 0.065 = 0.262$  m<sup>2</sup>

$A_h/A_p = 0.038/0.262 = 0.145$

From Figure 11.33,  $l_p/d_h = 2.6$ ; satisfactory, within 2.5 to 4.0.

### Number of holes

Area of one hole =  $1.964 \times 10^{-5}$  m<sup>2</sup>

Number of holes =  $\frac{0.038}{1.964 \times 10^{-5}} = 1935$

### Plate specification

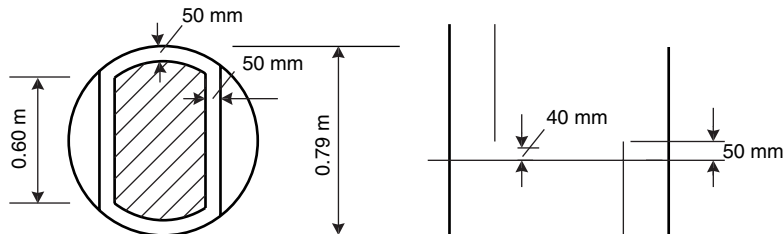


Plate No.	1	Turn-down	70 per cent max rate
Plate I.D.	0.79 m	Plate material	Mild steel
Hole size	5 mm	Downcomer material	Mild steel
Hole pitch	12.5 mm $\Delta$	Plate spacing	0.5 m
Total no. holes	—	Plate thickness	5 mm
Active holes	1935	Plate pressure drop	140 mm liquid = 1.3 kPa
Blanking area	—		

**Example 11.12**

For the plate design in Example 11.11, estimate the plate efficiency for the plate on which the concentration of acetone is 5 mol per cent. Use the AIChE method.

**Solution**

Plate will be in the stripping section (see Figure 11.7).

Plate dimensions:

$$\text{active area} = 0.38 \text{ m}^2,$$

$$\text{length between downcomers (Figure 11.32) (liquid path, } Z_L) = 0.79 - 2 \times 0.134 = 0.52 \text{ m},$$

$$\text{weir height} = 50 \text{ mm}.$$

Flow rates, check efficiency at minimum rates, at column base:

$$\text{vapour} = 0.7 \frac{162.3}{3600} = 0.032 \text{ kmol/s}$$

$$\text{liquid} = 0.7 \frac{811.6}{3600} = 0.158 \text{ kmol/s}$$

from the McCabe-Thiele diagram (Figure 11.7) at  $x = 0.05$ , assuming 60 per cent plate efficiency,  $y \approx 0.4$ . The liquid composition,  $x = 0.05$ , will occur on around the ninth plate from the bottom, the seventh from the top of the column. The pressure on this plate will be approximately:

$$9 \times 138 \times 10^{-3} \times 1000 \times 982 + 101.4 \times 10^3 = 113.6 \text{ kPa}$$

$$\text{say, } 1.14 \text{ bar}$$

At this pressure the plate temperature will be  $79^\circ\text{C}$ , and the liquid and vapour physical properties, from PPDS:

*liquid*

$$\text{mol. weight} = 20.02, \quad \rho_L = 925 \text{ kg/m}^3, \quad \mu_L = 9.34 \times 10^{-3} \text{ Nm}^{-2} \text{ s},$$

$$\sigma = 60 \times 10^{-3} \text{ N/m}$$

*vapour*

$$\text{mol. weight} = 34.04, \quad \rho_v = 1.35 \text{ kg/m}^3, \quad \mu_v = 10.0 \times 10^{-6} \text{ Nm}^{-2} \text{ s},$$

$$D_L = 4.64 \times 10^{-9} \text{ m}^2/\text{s} \text{ (estimated using Wilke-Chang equation, Chapter 8)}$$

$$D_v = 18.6 \times 10^{-6} \text{ m}^2/\text{s} \text{ (estimated using Fuller equation, Chapter 8)}$$

$$\text{Vapour, volumetric flow-rate} = \frac{0.032 \times 34.04}{1.35} = 0.81 \text{ m}^3/\text{s}$$

$$\text{Liquid, volumetric flow-rate} = \frac{0.158 \times 20.02}{925} = 3.42 \times 10^{-3} \text{ m}^3/\text{s}$$

$$u_a = \frac{0.81}{0.38} = 2.13 \text{ m/s}$$

$$F_v = u_a \sqrt{\rho_v} = \sqrt{2.13} \text{ m/s}$$

Average width over active surface =  $0.38/0.52 = 0.73 \text{ m}$

$$L = \frac{3.42 \times 10^{-3}}{0.73} = 4.69 \times 10^{-3} \text{ m}^2/\text{s}$$

$$N_G = \frac{(0.776 + 4.57 \times 10^{-3} \times 50 - 0.24 \times 2.48 + 105 \times 4.69 \times 10^{-3})}{\left(\frac{10.0 \times 10^{-6}}{1.35 \times 18.8 \times 10^{-6}}\right)^{1/2}}$$

$$= 1.44 \quad (11.71)$$

$$Z_c = 0.006 + 0.73 \times 10^{-3} \times 50 - 0.24 \times 10^{-3} \times 2.48 \times 50 + 1.22$$

$$\times 4.69 \times 10^{-3} = 18.5 \times 10^{-3} \text{ m}^3/\text{m}^2 \quad (11.75)$$

$$t_L = \frac{18.5 \times 10^{-3} \times 0.52}{4.69 \times 10^{-3}} = 2.05 \text{ s} \quad (11.73)$$

$$N_L = (4.13 \times 10^8 \times 4.64 \times 10^{-9})^{0.5} \times (0.21 \times 2.48 + 0.15) \times 2.05 = 1.9 \quad (11.72)$$

$$D_e = (0.0038 + 0.017 \times 2.13 + 3.86 \times 4.69 \times 10^{-3} + 0.18 \times 10^{-3} \times 50)^2$$

$$= 0.0045 \text{ m}^2/\text{s} \quad (11.77)$$

$$P_e = \frac{0.52^2}{0.0045 \times 2.05} = 29.3 \quad (11.76)$$

From the McCabe-Thiele diagram, at  $x = 0.05$ , the slope of the equilibrium line = 1.0.

$$V/L = 0.032/0.158 = 0.20$$

$$\text{so, } \frac{mV}{L} = 1.0 \times 0.20 = 0.20$$

$$\frac{\left(\frac{mV}{L}\right)}{N_L} = \frac{0.20}{1.9} = 0.11$$

From Figure 11.15  $E_{mv} = 0.70$

$$\frac{mV}{L} \cdot E_{mv} = 0.2 \times 0.58 = 0.12$$

From Figure 11.16  $E_{mV}/E_{mv} = 1.02$

$$E_{mV} = 0.70 \times 1.02 = 0.714$$

So plate efficiency = 71 per cent.

*Note:* The slope of the equilibrium line is difficult to determine at  $x = 0.05$ , but any error will not greatly affect the value of  $E_{mV}$ .

**Example 11.13**

Calculate the plate efficiency for the plate design considered in Examples 11.11 and 11.12, using Van Winkle's correlation.

**Solution**

From Examples 11.12 and 11.11:

$$\rho_L = 925 \text{ kg/m}^3,$$

$$\rho_v = 1.35 \text{ kg/m}^3,$$

$$\mu_L = 0.34 \times 10^{-3} \text{ Ns/m}^2,$$

$$\mu_v = 10.0 \times 10^{-6} \text{ Ns/m}^2,$$

$$D_{LK} = D_L = 4.64 \times 10^{-9} \text{ m}^2/\text{s},$$

$$h_w = 50 \text{ mm},$$

$$FA \text{ (fractional area)} = A_h/A_c = \frac{0.038}{0.50} = 0.076,$$

$$u_v = \text{superficial vapour velocity} = \frac{0.81}{0.50} = 1.62 \text{ m/s},$$

$$\sigma_L = 60 \times 10^{-3} \text{ N/m}$$

$$Dg = \left( \frac{60 \times 10^{-3}}{0.34 \times 10^{-3} \times 1.62} \right) = 109$$

$$Sc = \left( \frac{0.34 \times 10^{-3}}{925 \times 4.64 \times 10^{-9}} \right) = 79,$$

$$Re = \left( \frac{50 \times 10^{-3} \times 1.62 \times 1.35}{0.34 \times 10^{-3} \times 0.076} \right) = 4232$$

$$E_{mV} = 0.07(109)^{0.14}(79)^{0.25}(4232)^{0.08} \quad (11.69)$$

$$= \underline{\underline{0.79}} \text{ (79 per cent)}$$

**11.14. PACKED COLUMNS**

Packed columns are used for distillation, gas absorption, and liquid-liquid extraction; only distillation and absorption will be considered in this section. Stripping (desorption) is the reverse of absorption and the same design methods will apply.

The gas liquid contact in a packed bed column is continuous, not stage-wise, as in a plate column. The liquid flows down the column over the packing surface and the gas or vapour, counter-currently, up the column. In some gas-absorption columns co-current flow is used. The performance of a packed column is very dependent on the maintenance of good liquid and gas distribution throughout the packed bed, and this is an important consideration in packed-column design.

A schematic diagram, showing the main features of a packed absorption column, is given in Figure 11.36. A packed distillation column will be similar to the plate columns shown in Figure 11.1, with the plates replaced by packed sections.

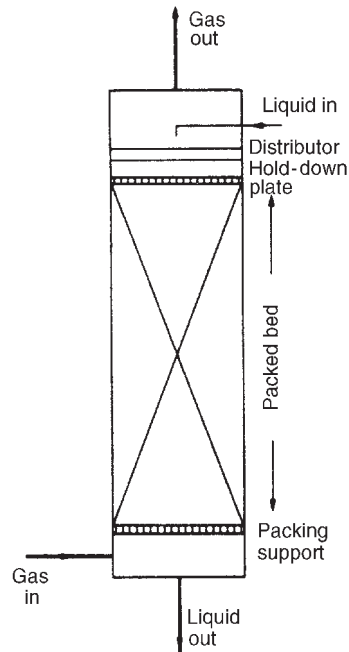


Figure 11.36. Packed absorption column

The design of packed columns using random packings is covered in books by Strigle (1994) and Billet (1995).

### ***Choice of plates or packing***

The choice between a plate or packed column for a particular application can only be made with complete assurance by costing each design. However, this will not always be worthwhile, or necessary, and the choice can usually be made, on the basis of experience by considering main advantages and disadvantages of each type; which are listed below:

1. Plate columns can be designed to handle a wider range of liquid and gas flow-rates than packed columns.
2. Packed columns are not suitable for very low liquid rates.
3. The efficiency of a plate can be predicted with more certainty than the equivalent term for packing (HETP or HTU).
4. Plate columns can be designed with more assurance than packed columns. There is always some doubt that good liquid distribution can be maintained throughout a packed column under all operating conditions, particularly in large columns.

5. It is easier to make provision for cooling in a plate column; coils can be installed on the plates.
6. It is easier to make provision for the withdrawal of side-streams from plate columns.
7. If the liquid causes fouling, or contains solids, it is easier to make provision for cleaning in a plate column; manways can be installed on the plates. With small-diameter columns it may be cheaper to use packing and replace the packing when it becomes fouled.
8. For corrosive liquids a packed column will usually be cheaper than the equivalent plate column.
9. The liquid hold-up is appreciably lower in a packed column than a plate column. This can be important when the inventory of toxic or flammable liquids needs to be kept as small as possible for safety reasons.
10. Packed columns are more suitable for handling foaming systems.
11. The pressure drop per equilibrium stage (HETP) can be lower for packing than plates; and packing should be considered for vacuum columns.
12. Packing should always be considered for small diameter columns, say less than 0.6 m, where plates would be difficult to install, and expensive.

### ***Packed-column design procedures***

The design of a packed column will involve the following steps:

1. Select the type and size of packing.
2. Determine the column height required for the specified separation.
3. Determine the column diameter (capacity), to handle the liquid and vapour flow rates.
4. Select and design the column internal features: packing support, liquid distributor, redistributors.

These steps are discussed in the following sections, and a packed-column design illustrated in Example 11.14.

#### **11.14.1. Types of packing**

The principal requirements of a packing are that it should:

- Provide a large surface area: a high interfacial area between the gas and liquid.
- Have an open structure: low resistance to gas flow.
- Promote uniform liquid distribution on the packing surface.
- Promote uniform vapour gas flow across the column cross-section.

Many diverse types and shapes of packing have been developed to satisfy these requirements. They can be divided into two broad classes:

1. Packings with a regular geometry: such as stacked rings, grids and proprietary structured packings.
2. Random packings: rings, saddles and proprietary shapes, which are dumped into the column and take up a random arrangement.

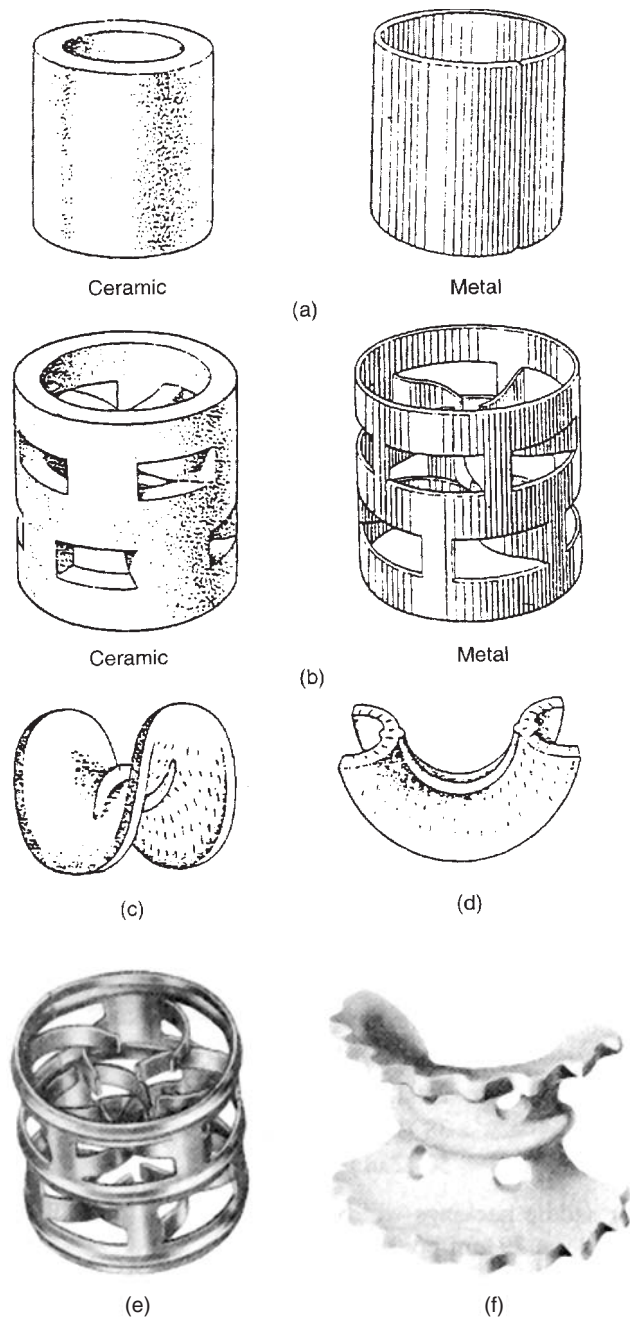


Figure 11.37. Types of packing (Norton Co.). (a) Raschig rings (b) Pall rings (c) Berl saddle ceramic (d) Intalox saddle ceramic (e) Metal Hypac (f) Ceramic, super Intalox

Grids have an open structure and are used for high gas rates, where low pressure drop is essential; for example, in cooling towers. Random packings and structured packing elements are more commonly used in the process industries.

### Random packing

The principal types of random packings are shown in Figure 11.37 (see p. 590). Design data for these packings are given in Table 11.2. Data on a wider range of packing sizes are given in Volume 2, Chapter 4. The design methods and data given in this section can be used for the preliminary design of packed columns, but for detailed design it is advisable to consult the packing manufacturer's technical literature to obtain data for the particular packing that will be used. The packing manufacturers should be consulted for details of the many special types of packing that are available for special applications.

Raschig rings, Figure 11.37*a*, are one of the oldest specially manufactured types of random packing, and are still in general use. Pall rings, Figure 11.37*b*, are essentially Raschig rings in which openings have been made by folding strips of the surface into the ring. This increases the free area and improves the liquid distribution characteristics. Berl saddles, Figure 11.37*c*, were developed to give improved liquid distribution compared to Raschig rings, Intalox saddles, Figure 11.37*d*, can be considered to be an improved type of Berl saddle; their shape makes them easier to manufacture than Berl saddles. The Hypac and Super Intalox packings shown in Figure 11.37*e, f* can be considered improved types of Pall ring and Intalox saddle, respectively.

Table 11.2. Design data for various packings

	Size		Bulk density (kg/m <sup>3</sup> )	Surface area <i>a</i> (m <sup>2</sup> /m <sup>3</sup> )	Packing factor <i>F<sub>p</sub></i> m <sup>-1</sup>
	in.	mm			
Raschig rings	0.50	13	881	368	2100
ceramic	1.0	25	673	190	525
	1.5	38	689	128	310
	2.0	51	651	95	210
	3.0	76	561	69	120
Metal	0.5	13	1201	417	980
(density for carbon steel)	1.0	25	625	207	375
	1.5	38	785	141	270
	2.0	51	593	102	190
	3.0	76	400	72	105
Pall rings	0.625	16	593	341	230
metal	1.0	25	481	210	160
(density for carbon steel)	1.25	32	385	128	92
	2.0	51	353	102	66
	3.5	76	273	66	52
Plastics	0.625	16	112	341	320
(density for polypropylene)	1.0	25	88	207	170
	1.5	38	76	128	130
	2.0	51	68	102	82
	3.5	89	64	85	52
Intalox saddles	0.5	13	737	480	660
ceramic	1.0	25	673	253	300
	1.5	38	625	194	170
	2.0	51	609	108	130
	3.0	76	577		72



Intalox saddles, Super Intalox and Hypac packings are proprietary design, and registered trade marks of the Norton Chemical Process Products Ltd.

Ring and saddle packings are available in a variety of materials: ceramics, metals, plastics and carbon. Metal and plastics (polypropylene) rings are more efficient than ceramic rings, as it is possible to make the walls thinner.

Raschig rings are cheaper per unit volume than Pall rings or saddles but are less efficient, and the total cost of the column will usually be higher if Raschig rings are specified. For new columns, the choice will normally be between Pall rings and Berl or Intalox saddles.

The choice of material will depend on the nature of the fluids and the operating temperature. Ceramic packing will be the first choice for corrosive liquids; but ceramics are unsuitable for use with strong alkalis. Plastics packings are attacked by some organic solvents, and can only be used up to moderate temperatures; so are unsuitable for distillation columns. Where the column operation is likely to be unstable metal rings should be specified, as ceramic packing is easily broken. The choice of packings for distillation and absorption is discussed in detail by Eckert (1963), Strigle (1994), Kister (1992) and Billet (1995).

### **Packing size**

In general, the largest size of packing that is suitable for the size of column should be used, up to 50 mm. Small sizes are appreciably more expensive than the larger sizes. Above 50 mm the lower cost per cubic metre does not normally compensate for the lower mass transfer efficiency. Use of too large a size in a small column can cause poor liquid distribution.

Recommended size ranges are:

Column diameter	Use packing size
<0.3 m (1 ft)	<25 mm (1 in.)
0.3 to 0.9 m (1 to 3 ft)	25 to 38 mm (1 to 1.5 in.)
>0.9 m	50 to 75 mm (2 to 3 in.)

### **Structured packing**

The term *structured packing* refers to packing elements made up from wire mesh or perforated metal sheets. The material is folded and arranged with a regular geometry, to give a high surface area with a high void fraction. A typical example is shown in Figure 11.38.

Structured packings are produced by a number of manufacturers. The basic construction and performance of the various proprietary types available are similar. They are available in metal, plastics and stoneware. The advantage of structured packings over random packing is their low HETP (typically less than 0.5 m) and low pressure drop (around 100 Pa/m). They are being increasingly used in the following applications:

1. For difficult separations, requiring many stages: such as the separation of isotopes.
2. High vacuum distillation.
3. For column revamps: to increase capacity and reduce reflux ratio requirements.

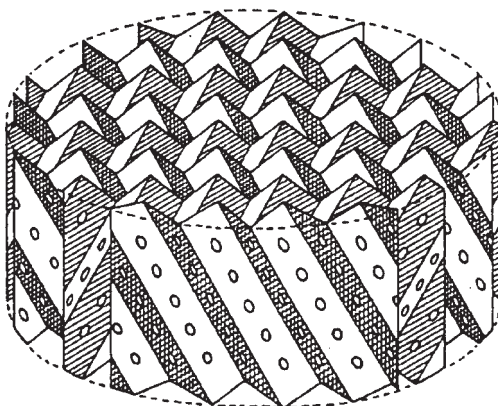


Figure 11.38. Make-up of structured packing. (Reproduced from Butcher (1988) with permission.)

The applications have mainly been in distillation, but structured packings can also be used in absorption; in applications where high efficiency and low pressure drop are needed.

The cost of structured packings per cubic metre will be significantly higher than that of random packings, but this is offset by their higher efficiency.

The manufacturers' technical literature should be consulted for design data. A review of the types available is given by Butcher (1988). Generalised methods for predicting the capacity and pressure drop of structured packings are given by Fair and Bravo (1990) and Kister and Gill (1992). The use of structured packings in distillation is discussed in detail in the book by Kister (1992).

### 11.14.2. Packed-bed height

#### *Distillation*

For the design of packed distillation columns it is simpler to treat the separation as a staged process, and use the concept of the height of an equivalent equilibrium stage to convert the number of ideal stages required to a height of packing. The methods for estimating the number of ideal stages given in Sections 11.5 to 11.8 can then be applied to packed columns.

The height of an equivalent equilibrium stage, usually called the height of a theoretical plate (HETP), is the height of packing that will give the same separation as an equilibrium stage. It has been shown by Eckert (1975) that in distillation the HETP for a given type and size of packing is essentially constant, and independent of the system physical properties; providing good liquid distribution is maintained and the pressure drop is at least above 17 mm water per metre of packing height. The following values for Pall rings can be used to make an approximate estimate of the bed height required.

Size, mm	HETP, m
25 (1 in.)	0.4–0.5
38 (1½ in.)	0.6–0.75
50 (2 in.)	0.75–1.0

The HETP for saddle packings will be similar to that for Pall rings providing the pressure drop is at least 29 mm per m.

The HETP for Raschig rings will be higher than those for Pall rings or saddles, and the values given above will only apply at an appreciably higher pressure drop, greater than 42 mm per m.

The methods for estimating the heights of transfer units, HTU, given in Section 11.14.3 can be used for distillation. The relationship between transfer units and the height of an equivalent theoretical plate, HETP is given by:

$$\text{HETP} = \frac{\mathbf{H}_{OG} \text{Ln} \left( \frac{mG_m}{L_m} \right)}{\left( \frac{mG_m}{L_m - 1} \right)} \quad (11.96)$$

from equation 11.105

$$\mathbf{H}_{OG} = \mathbf{H}_G + \left( \frac{mG_m}{L_m} \right) \mathbf{H}_L$$

The slope of the operating line  $m$  will normally vary throughout a distillation so it will be necessary to calculate the HETP for each plate or a series of plates.

### **Absorption**

Though packed absorption and stripping columns can also be designed as staged process, it is usually more convenient to use the integrated form of the differential equations set up by considering the rates of mass transfer at a point in the column. The derivation of these equations is given in Volume 2, Chapter 12.

Where the concentration of the solute is small, say less than 10 per cent, the flow of gas and liquid will be essentially constant throughout the column, and the height of packing required,  $Z$ , is given by:

$$Z = \frac{G_m}{K_G a P} \int_{y_2}^{y_1} \frac{dy}{y - y_e} \quad (11.97)$$

in terms of the overall gas phase mass transfer coefficient  $K_G$  and the gas composition. Or,

$$Z = \frac{L_m}{K_L a C_t} \int_{x_2}^{x_1} \frac{dx}{x_e - x} \quad (11.98)$$

in terms of the overall liquid-phase mass-transfer coefficient  $K_L$  and the liquid composition,

where  $G_m$  = molar gas flow-rate per unit cross-sectional area,

$L_m$  = molar liquid flow-rate per unit cross-sectional area,

$a$  = interfacial surface area per unit volume,

$P$  = total pressure,

$C_t$  = total molar concentration,

$y_1$  and  $y_2$  = the mol fractions of the solute in the gas at the bottom and top of the column, respectively,

$x_1$  and  $x_2$  = the mol fractions of the solute in the liquid at the bottom and top of the column, respectively,

$x_e$  = the concentration in the liquid that would be in equilibrium with the gas concentration at any point,

$y_e$  = the concentration in the gas that would be in equilibrium with the liquid concentration at any point.

The relation between the equilibrium concentrations and actual concentrations is shown in Figure 11.39.

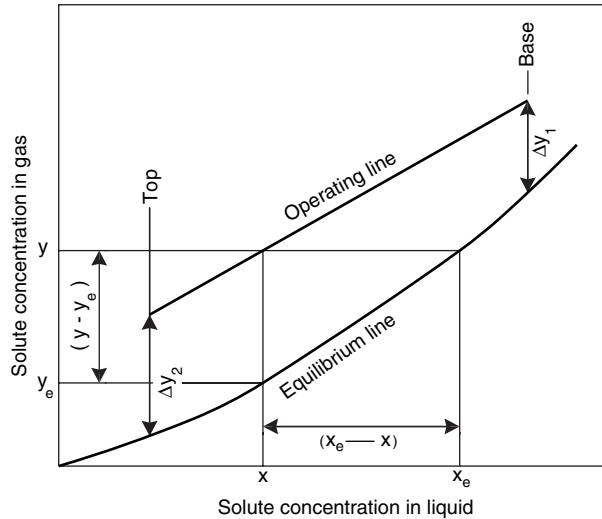


Figure 11.39. Gas absorption concentration relationships

For design purposes it is convenient to write equations 11.97 and 11.98 in terms of “transfer units” (HTU); where the value of integral is the number of transfer units, and the group in front of the integral sign, which has units of length, is the height of a transfer unit.

$$Z = \mathbf{H}_{OG} \mathbf{N}_{OG} \quad (11.99a)$$

or 
$$Z = \mathbf{H}_{OL} \mathbf{N}_{OL} \quad (11.99b)$$

where  $\mathbf{H}_{OG}$  is the height of an overall gas-phase transfer unit

$$= \frac{G_m}{K_G a P} \quad (11.100)$$

$\mathbf{N}_{OG}$  is the number of overall gas-phase transfer units

$$= \int_{y_2}^{y_1} \frac{dy}{y - y_e} \quad (11.101)$$

$\mathbf{H}_{OL}$  is the height of an overall liquid-phase transfer unit

$$= \frac{L_m}{K_L a C_t} \quad (11.102)$$

$N_{OL}$  is the number of overall liquid-phase transfer units

$$= \int_{x_2}^{x_1} \frac{dx}{x_e - x} \quad (11.103)$$

The number of overall gas-phase transfer units is often more conveniently expressed in terms of the partial pressure of the solute gas.

$$N_{OG} = \int_{p_1}^{p_2} \frac{dp}{p - p_e} \quad (11.104)$$

The relationship between the overall height of a transfer unit and the individual film transfer units  $H_L$  and  $H_G$ , which are based on the concentration driving force across the liquid and gas films, is given by:

$$H_{OG} = H_G + m \frac{G_m}{L_m} H_L \quad (11.105)$$

$$H_{OL} = H_L + \frac{L_m}{mG_m} H_G \quad (11.106)$$

where  $m$  is the slope of the equilibrium line and  $G_m/L_m$  the slope of the operating line.

The number of transfer units is obtained by graphical or numerical integration of equations 11.101, 11.103 or 11.104.

Where the operating and equilibrium lines are straight, and they can usually be considered to be so for dilute systems, the number of transfer units is given by:

$$N_{OG} = \frac{y_1 - y_2}{\Delta y_{lm}} \quad (11.107)$$

where  $\Delta y_{lm}$  is the log mean driving force, given by:

$$y_{lm} = \frac{\Delta y_1 - \Delta y_2}{\ln \left( \frac{\Delta y_1}{\Delta y_2} \right)} \quad (11.108)$$

where  $\Delta y_1 = y_1 - y_e$ ,

$\Delta y_2 = y_2 - y_e$ .

If the equilibrium curve and operating lines can be taken as straight and the solvent feed essentially solute free, the number of transfer units is given by:

$$N_{OG} = \frac{1}{1 - \left( \frac{mG_m}{L_m} \right)} \ln \left[ \left( 1 - \frac{mG_m}{L_m} \right) \frac{y_1}{y_2} + \frac{mG_m}{L_m} \right] \quad (11.109)$$

This equation is plotted in Figure 11.40, which can be used to make a quick estimate of the number of transfer units required for a given separation.

It can be seen from Figure 11.40 that the number of stages required for a given separation is very dependent on the flow rate  $L_m$ . If the solvent rate is not set by

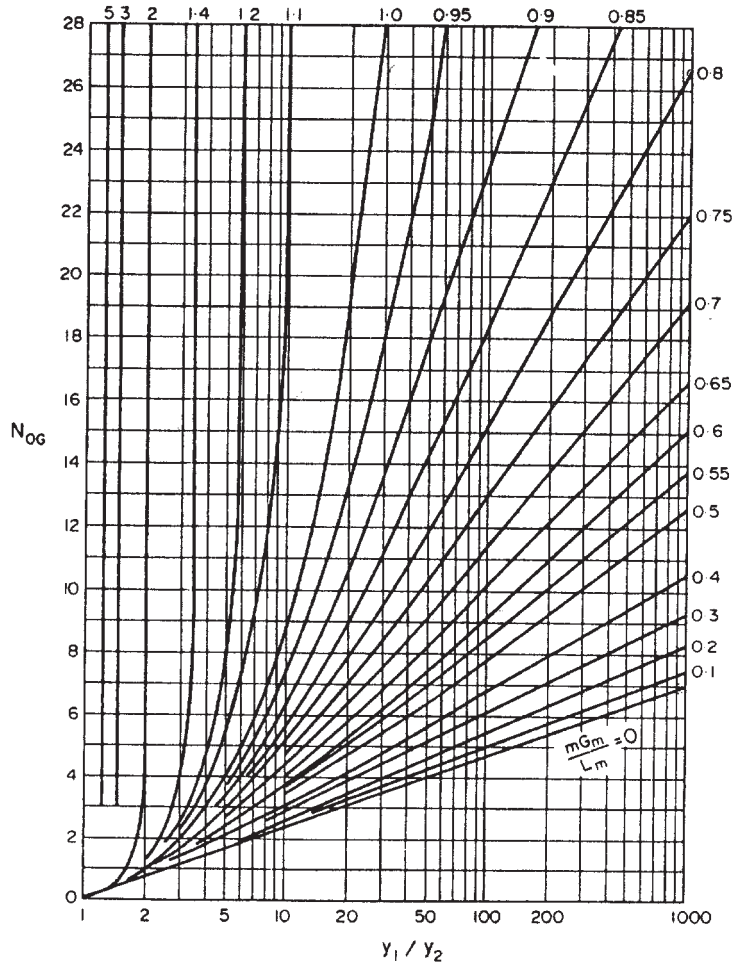


Figure 11.40. Number of transfer units  $N_{OG}$  as a function of  $y_1/y_2$  with  $mG_m/L_m$  as parameter

other process considerations, Figure 11.40 can be used to make quick estimates of the column height at different flow rates to find the most economic value. Colburn (1939) has suggested that the optimum value for the term  $mG_m/L_m$  will lie between 0.7 to 0.8.

Only physical absorption from dilute gases has been considered in this section. For a discussion of absorption from concentrated gases and absorption with chemical reaction, the reader should refer to Volume 2, or to the book by Treybal (1980). If the inlet gas concentration is not too high, the equations for dilute systems can be used by dividing the operating line up into two or three straight sections.

### 11.14.3. Prediction of the height of a transfer unit (HTU)

There is no entirely satisfactory method for predicting the height of a transfer unit. In practice the value for a particular packing will depend not only on the physical properties

and flow-rates of the gas and liquid, but also on the uniformity of the liquid distribution throughout the column, which is dependent on the column height and diameter. This makes it difficult to extrapolate data obtained from small size laboratory and pilot plant columns to industrial size columns. Whenever possible estimates should be based on actual values obtained from operating columns of similar size to that being designed.

Experimental values for several systems are given by Cornell *et al.* (1960), Eckert (1963), and Vital *et al.* (1984). A selection of values for a range of systems is given in Table 11.3. The composite mass transfer term  $K_G a$  is normally used when reporting experimental mass-transfer coefficients for packing, as the effective interfacial area for mass transfer will be less than the actual surface area  $a$  of the packing.

Many correlations have been published for predicting the height of a transfer unit, and the mass-transfer coefficients; several are reviewed in Volume 2, Chapter 12. The two methods given in this section have been found to be reliable for preliminary design work, and, in the absence of practical values, can be used for the final design with a suitable factor of safety.

The approach taken by the authors of the two methods is fundamentally different, and this provides a useful cross-check on the predicted values. Judgement must always be used when using predictive methods in design, and it is always worthwhile trying several methods and comparing the results.

Typical values for the HTU of random packings are:

25 mm (1 in.)	0.3 to 0.6 m (1 to 2 ft)
38 mm ( $1\frac{1}{2}$ in.)	0.5 to 0.75 m ( $1\frac{1}{2}$ to $2\frac{1}{2}$ ft)
50 mm (2 in.)	0.6 to 1.0 m (2 to 3 ft)

Table 11.3. Typical packing efficiencies

System	Pressure kPa	Column dia, m	Packing type	Packing size, mm	HTU m	HETP m
<i>Absorption</i>						
Hydrocarbons	6000	0.9	Pall	50		0.85
NH <sub>3</sub> -Air-H <sub>2</sub> O	101	—	Berl	50	0.50	
Air-water	101	—	Berl	50	0.50	
Acetone-water	101	0.6	Pall	50		0.75
<i>Distillation</i>						
Pentane-propane	101	0.46	Pall	25		0.46
IPA-water	101	0.46	Int.	25	0.75	0.50
Methanol-water	101	0.41	Pall	25	0.52	
	101	0.20	Int.	25		0.46
Acetone-water	101	0.46	Pall	25		0.37
	101	0.36	Int.	25		0.46
Formic acid-water	101	0.91	Pall	50		0.45
Acetone-water	101	0.38	Pall	38	0.55	0.45
	101	0.38	Int.	50	0.50	0.45
	101	1.07	Int.	38		1.22
MEK-toluene	101	0.38	Pall	25	0.29	0.35
	101	0.38	Int.	25	0.27	0.23
	101	0.38	Berl	25	0.31	0.31

Pall = Pall rings, Berl = Berl saddles, Int. = Intalox saddles

### Cornell's method

Cornell *et al.* (1960) reviewed the previously published data and presented empirical equations for predicting the height of the gas and liquid film transfer units. Their correlation takes into account the physical properties of the system, the gas and liquid flow-rates; and the column diameter and height. Equations and figures are given for a range of sizes of Raschig rings and Berl saddles. Only those for Berl saddles are given here, as it is unlikely that Raschig rings would be considered for a new column. Though the mass-transfer efficiency of Pall rings and Intalox saddles will be higher than that of the equivalent size Berl saddle, the method can be used to make conservative estimates for these packings.

Bolles and Fair (1982) have extended the correlations given in the earlier paper to include metal Pall rings.

Cornell's equations are:

$$\mathbf{H}_G = 0.011\psi_h(Sc)_v^{0.5} \left(\frac{D_c}{0.305}\right)^{1.11} \left(\frac{Z}{3.05}\right)^{0.33} / (L_w^* f_1 f_2 f_3)^{0.5} \quad (11.110)$$

$$\mathbf{H}_L = 0.305\phi_h(Sc)_L^{0.5} K_3 \left(\frac{Z}{3.05}\right)^{0.15} \quad (11.111)$$

where  $\mathbf{H}_G$  = height of a gas-phase transfer unit, m,

$\mathbf{H}_L$  = height of a liquid-phase transfer unit, m,

$(Sc)_v$  = gas Schmidt number =  $(\mu_v/\rho_v D_v)$ ,

$(Sc)_L$  = liquid Schmidt number =  $(\mu_L/\rho_L D_L)$ ,

$D_c$  = column diameter, m,

$Z$  = column height, m,

$K_3$  = percentage flooding correction factor, from Figure 11.41,

$\psi_h$  =  $\mathbf{H}_G$  factor from Figure 11.42,

$\phi_h$  =  $\mathbf{H}_L$  factor from Figure 11.43,

$L_w^*$  = liquid mass flow-rate per unit area column cross-sectional area, kg/m<sup>2</sup>s,

$f_1$  = liquid viscosity correction factor =  $(\mu_L/\mu_w)^{0.16}$ ,

$f_2$  = liquid density correction factor =  $(\rho_w/\rho_L)^{1.25}$ ,

$f_3$  = surface tension correction factor =  $(\sigma_w/\sigma_L)^{0.8}$ ,

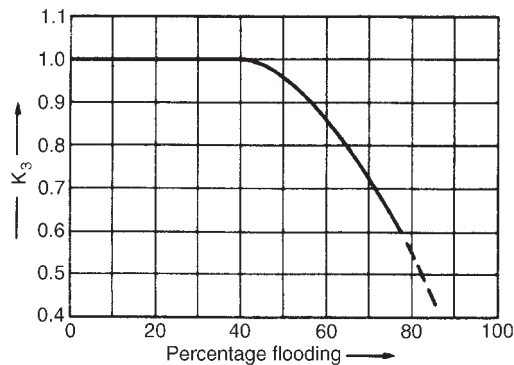
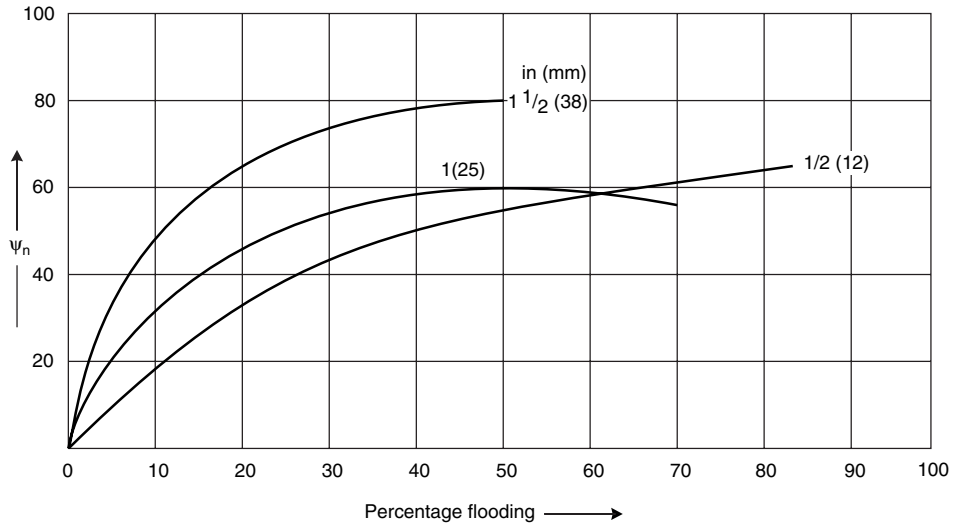
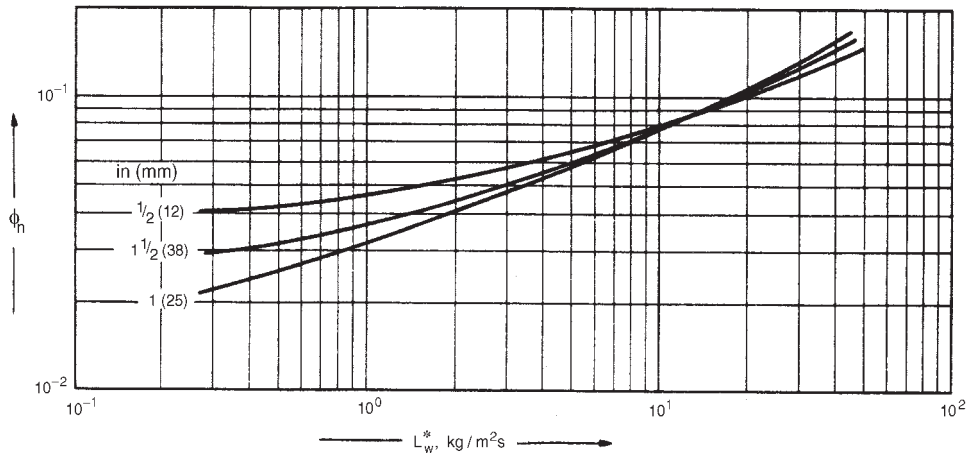


Figure 11.41. Percentage flooding correction factor



Figure 11.42. Factor for  $H_G$  for Berl saddlesFigure 11.43. Factor for  $H_L$  for Berl saddles

where the suffix  $w$  refers to the physical properties of water at 20°C; all other physical properties are evaluated at the column conditions.

The terms  $(D_c/0.305)$  and  $(Z/3.05)$  are included in the equations to allow for the effects of column diameter and packed-bed height. The “standard” values used by Cornell were 1 ft (0.305 m) for diameter, and 10 ft (3.05 m) for height. These correction terms will clearly give silly results if applied over too wide a range of values. For design purposes the diameter correction term should be taken as a fixed value of 2.3 for columns above 0.6 m

(2 ft) diameter, and the height correction should only be included when the distance between liquid redistributors is greater than 3 m. To use Figures 11.41 and 11.42 an estimate of the column percentage flooding is needed. This can be obtained from Figure 11.44, where a flooding line has been included with the lines of constant pressure drop.

$$\text{Percentage flooding} = \left[ \frac{K_4 \text{ at design pressure drop}}{K_4 \text{ at flooding}} \right]^{1/2} \quad (11.112)$$

A full discussion of flooding in packed columns is given in Volume 2, Chapter 4.

### **Onda's method**

Onda *et al.* (1968) published useful correlations for the film mass-transfer coefficients  $k_G$  and  $k_L$  and the effective wetted area of the packing  $a_w$ , which can be used to calculate  $\mathbf{H}_G$  and  $\mathbf{H}_L$ .

Their correlations were based on a large amount of data on gas absorption and distillation; with a variety of packings, which included Pall rings and Berl saddles. Their method for estimating the effective area of packing can also be used with experimentally determined values of the mass-transfer coefficients, and values predicted using other correlations.

The equation for the effective area is:

$$\frac{a_w}{a} = 1 - \exp \left[ -1.45 \left( \frac{\sigma_c}{\sigma_L} \right)^{0.75} \left( \frac{L_w^*}{a\mu_L} \right)^{0.1} \left( \frac{L_w^{*2}a}{\rho_L^2} \right)^{-0.05} \left( \frac{L_w^{*2}}{\rho_L\sigma_L a} \right)^{0.2} \right] \quad (11.113)$$

and for the mass coefficients:

$$k_L \left( \frac{\rho_L}{\mu_L g} \right)^{1/3} = 0.0051 \left( \frac{L_w^*}{a_w\mu_L} \right)^{2/3} \left( \frac{\mu_L}{\rho_L D_L} \right)^{-1/2} (ad_p)^{0.4} \quad (11.114)$$

$$\frac{k_G RT}{a D_v} = K_5 \left( \frac{V_w^*}{a\mu_v} \right)^{0.7} \left( \frac{\mu_v}{\rho_v D_v} \right)^{1/3} (ad_p)^{-2.0} \quad (11.115)$$

where  $K_5 = 5.23$  for packing sizes above 15 mm, and 2.00 for sizes below 15 mm,

$L_w^*$  = liquid mass flow rate per unit cross-sectional area, kg/m<sup>2</sup>s,

$V_w^*$  = gas mass flow rate per unit column cross-sectional area, kg/m<sup>2</sup>s,

$a_w$  = effective interfacial area of packing per unit volume, m<sup>2</sup>/m<sup>3</sup>,

$a$  = actual area of packing per unit volume (see Table 11.3), m<sup>2</sup>/m<sup>3</sup>,

$d_p$  = packing size, m,

$\sigma_c$  = critical surface tension for the particular packing material given below:

Material	$\sigma_c$ mN/m
Ceramic	61
Metal (steel)	75
Plastic (polyethylene)	33
Carbon	56

$\sigma_L$  = liquid surface tension, N/m,

$k_G$  = gas film mass transfer coefficient, kmol/m<sup>2</sup>s atm or kmol/m<sup>2</sup>s bar,

$k_L$  = liquid film mass transfer coefficient, kmol/m<sup>2</sup>s (kmol/m<sup>3</sup>) = m/s.

*Note:* all the groups in the equations are dimensionless.

The units for  $k_G$  will depend on the units used for the gas constant:

$$\mathbf{R} = 0.08206 \text{ atm m}^3/\text{kmol K or}$$

$$0.08314 \text{ bar m}^3/\text{kmol K}$$

The film transfer unit heights are given by:

$$\mathbf{H}_G = \frac{G_m}{k_G a_w P} \quad (11.116)$$

$$\mathbf{H}_L = \frac{L_m}{k_L a_w C_t} \quad (11.117)$$

where  $P$  = column operating pressure, atm or bar,

$C_t$  = total concentration, kmol/m<sup>3</sup> =  $\rho_L$ /molecular weight solvent,

$G_m$  = molar gas flow-rate per unit cross-sectional area, kmol/m<sup>2</sup>s,

$L_m$  = molar liquid flow-rate per unit cross-sectional area, kmol/m<sup>2</sup>s.

### **Nomographs**

A set of nomographs are given in Volume 2, Chapter 12 for the estimation of  $\mathbf{H}_G$  and  $\mathbf{H}_L$ , and the wetting rate. These were taken from a proprietary publication, but are based on a set of similar nomographs given by Czermann *et al.* (1958), who developed the nomographs from correlations put forward by Morris and Jackson (1953) and other workers.

The nomographs can be used to make a quick, rough, estimate of the column height, but are an oversimplification, as they do not take into account all the physical properties and other factors that affect mass transfer in packed columns.

#### **11.14.4. Column diameter (capacity)**

The capacity of a packed column is determined by its cross-sectional area. Normally, the column will be designed to operate at the highest economical pressure drop, to ensure good liquid and gas distribution. For random packings the pressure drop will not normally exceed 80 mm of water per metre of packing height. At this value the gas velocity will be about 80 per cent of the flooding velocity. Recommended design values, mm water per m packing, are:

Absorbers and strippers	15 to 50
Distillation, atmospheric and moderate pressure	40 to 80

Where the liquid is likely to foam, these values should be halved.

For vacuum distillations the maximum allowable pressure drop will be determined by the process requirements, but for satisfactory liquid distribution the pressure drop should not be less than 8 mm water per m. If very low bottom pressures are required special low pressure-drop gauze packings should be considered; such as Hyperfil, Multifil or Dixon rings; see Volume 2, Chapter 4.

The column cross-sectional area and diameter for the selected pressure drop can be determined from the generalised pressure-drop correlation given in Figure 11.44.

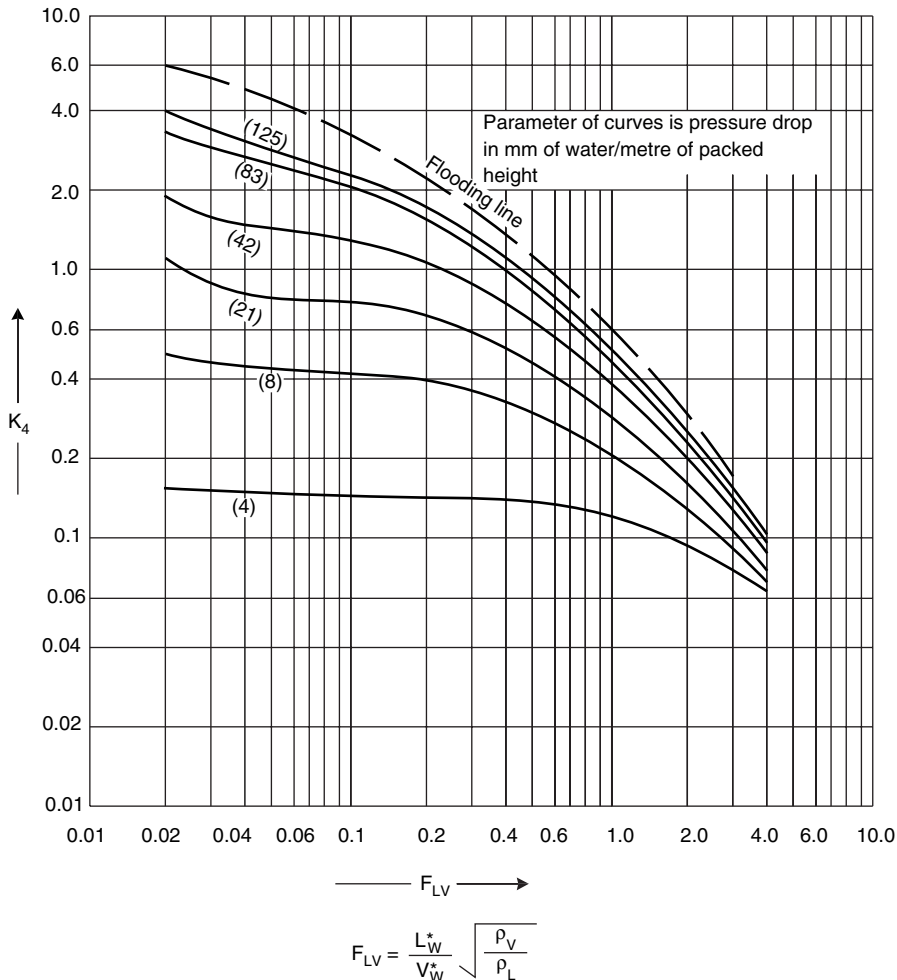


Figure 11.44. Generalised pressure drop correlation, adapted from a figure by the Norton Co. with permission

Figure 11.44 correlates the liquid and vapour flow rates, system physical properties and packing characteristics, with the gas mass flow-rate per unit cross-sectional area; with lines of constant pressure drop as a parameter.

The term  $K_4$  on Figure 11.44 is the function:

$$K_4 = \frac{13.1(V_w^*)^2 F_p \left(\frac{\mu_L}{\rho_L}\right)^{0.1}}{\rho_v(\rho_L - \rho_v)} \quad (11.118)$$

where  $V_w^*$  = gas mass flow-rate per unit column cross-sectional area,  $\text{kg/m}^2\text{s}$

$F_p$  = packing factor, characteristic of the size and type of packing,  
see Table 11.3,  $\text{m}^{-1}$ .

$\mu_L$  = liquid viscosity,  $\text{Ns/m}^2$

$\rho_L, \rho_v$  = liquid and vapour densities,  $\text{kg/m}^3$

The values of the flow factor  $F_{LV}$  given in Figure 11.44 covers the range that will generally give satisfactory column performance.

The ratio of liquid to gas flow will be fixed by the reflux ratio in distillation; and in gas absorption will be selected to give the required separation with the most economic use of solvent.

A new generalised correlation for pressure drop in packed columns, similar to Figure 11.44, has been published by Leva (1992), (1995). The new correlations gives a better prediction for systems where the density of the irrigating fluid is appreciably greater than that of water. It can also be used to predict the pressure drop over dry packing.

### Example 11.14

Sulphur dioxide produced by the combustion of sulphur in air is absorbed in water. Pure  $\text{SO}_2$  is then recovered from the solution by steam stripping. Make a preliminary design for the absorption column. The feed will be 5000  $\text{kg/h}$  of gas containing 8 per cent v/v  $\text{SO}_2$ . The gas will be cooled to  $20^\circ\text{C}$ . A 95 per cent recovery of the sulphur dioxide is required.

### Solution

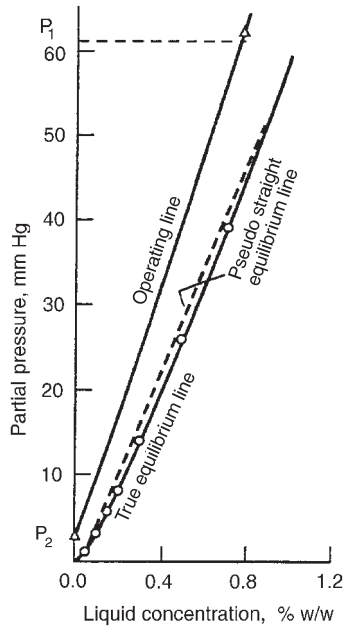
As the solubility of  $\text{SO}_2$  in water is high, operation at atmospheric pressure should be satisfactory. The feed-water temperature will be taken as  $20^\circ\text{C}$ , a reasonable design value.

### Solubility data

From *Chemical Engineers Handbook*, 5th edn, McGraw-Hill, 1973.

per cent w/w solution	0.05	0.1	0.15	0.2	0.3	0.5	0.7	1.0	1.5
$\text{SO}_2$									
Partial press. gas mmHg	1.2	3.2	5.8	8.5	14.1	26	39	59	92

Partial pressure of  $\text{SO}_2$  in the feed =  $(8/100) \times 760 = 60.8 \text{ mm Hg}$

Figure (d). SO<sub>2</sub> absorber design (Example 11.14)

These figures are plotted in Figure (d).

### Number of stages

Partial pressure in the exit gas at 95 per cent recovery =  $60.8 \times 0.05 = 3.04$  mm Hg

Over this range of partial pressure the equilibrium line is essentially straight so Figure 11.40 can be used to estimate the number of stages needed.

The use of Figure 11.40 will slightly overestimate the number of stages and a more accurate estimate would be made by graphical integration of equation 11.104; but this is not justified in view of the uncertainty in the prediction of the transfer unit height.

Molecular weights: SO<sub>2</sub> = 64, H<sub>2</sub>O = 18, air = 29

### Slope of equilibrium line

From the data: partial pressure at 1.0% w/w SO<sub>2</sub> = 59 mm Hg.

$$\text{Mol. fraction in vapour} = \frac{59}{760} = 0.0776$$

$$\text{Mol. fraction in liquid} = \frac{\frac{1}{64}}{\frac{1}{64} + \frac{99}{18}} = 0.0028$$

$$m = \frac{0.0776}{0.0028} = 27.4$$

To decide the most economic water flow-rate, the stripper design should be considered together with the absorption design, but for the purpose of this example the absorption design will be considered alone. Using Figure 11.40 the number of stages required at different water rates will be determined and the “optimum” rate chosen:

$$\frac{y_1}{y_2} = \frac{p_1}{p_2} = \frac{60.8}{3.04} = 20$$

$m \frac{G_m}{L_m}$	0.5	0.6	0.7	0.8	0.9	1.0
$N_{OG}$	3.7	4.1	6.3	8	10.8	19.0

It can be seen that the “optimum” will be between  $mG_m/L_m = 0.6$  to  $0.8$ , as would be expected. Below  $0.6$  there is only a small decrease in the number of stages required with increasing liquid rate; and above  $0.8$  the number of stages increases rapidly with decreasing liquid rate.

Check the liquid outlet composition at  $0.6$  and  $0.8$ :

$$\text{Material balance } L_m x_1 = G_m (y_1 - y_2)$$

$$\text{so } x_1 = \frac{G_m}{L_m} (0.08 \times 0.95) = \frac{m}{27.4} \frac{G_m}{L_m} (0.076)$$

$$\text{at } \frac{mG_m}{L_m} = 0.6, x_1 = 1.66 \times 10^{-3} \text{ mol fraction}$$

$$\text{at } \frac{mG_m}{L_m} = 0.8, x_1 = 2.22 \times 10^{-3} \text{ mol fraction}$$

Use  $0.8$ , as the higher concentration will favour the stripper design and operation, without significantly increasing the number of stages needed in the absorber.

$$N_{OG} = \underline{\underline{8}}$$

### Column diameter

The physical properties of the gas can be taken as those for air, as the concentration of  $\text{SO}_2$  is low.

$$\text{Gas flow-rate} = \frac{5000}{3600} = 1.39 \text{ kg/s}, = \frac{1.39}{29} = 0.048 \text{ kmol/s}$$

$$\begin{aligned} \text{Liquid flow-rate} &= \frac{27.4}{0.8} \times 0.048 = 1.64 \text{ kmol/s} \\ &= 29.5 \text{ kg/s.} \end{aligned}$$

Select 38 mm ( $1\frac{1}{2}$  in.) ceramic Intalox saddles.

From Table 11.3,  $F_p = 170 \text{ m}^{-1}$

$$\text{Gas density at } 20^\circ\text{C} = \frac{29}{22.4} \times \frac{273}{293} = 1.21 \text{ kg/m}^3$$

$$\text{Liquid density} \simeq 1000 \text{ kg/m}^3$$

$$\text{Liquid viscosity} = 10^{-3} \text{ Ns/m}^2$$

$$\frac{L_W^*}{V_W^*} \sqrt{\frac{\rho_v}{\rho_L}} = \frac{29.5}{1.39} \sqrt{\frac{1.21}{10^3}} = 0.74$$

Design for a pressure drop of 20 mm H<sub>2</sub>O/m packing

From Figure 11.44,

$$K_4 = 0.35$$

At flooding  $K_4 = 0.8$

$$\text{Percentage flooding} = \sqrt{\frac{0.35}{0.8}} \times 100 = 66 \text{ per cent, satisfactory.}$$

From equation 11.118

$$\begin{aligned} V_W^* &= \left[ \frac{K_4 \rho_V (\rho_L - \rho_v)}{13.1 F_p (\mu_L / \rho_L)^{0.1}} \right]^{1/2} \\ &= \left[ \frac{0.35 \times 1.21 (1000 - 1.21)}{13.1 \times 170 (10^{-3} / 10^3)^{0.1}} \right]^{1/2} = 0.87 \text{ kg/m}^2\text{s} \end{aligned}$$

$$\text{Column area required} = \frac{1.39}{0.87} = 1.6 \text{ m}^2$$

$$\text{Diameter} = \sqrt{\frac{4}{\pi}} \times 1.6 = 1.43 \text{ m}$$

Round off to 1.50 m

$$\text{Column area} = \frac{\pi}{4} \times 1.5^2 = 1.77 \text{ m}^2$$

$$\text{Packing size to column diameter ratio} = \frac{1.5}{38 \times 10^{-3}} = 39,$$

A larger packing size could be considered.

Percentage flooding at selected diameter

$$= 66 \times \frac{1.6}{1.77} = 60 \text{ per cent,}$$

Could consider reducing column diameter.

## **Estimation of H<sub>OG</sub>**

### **Cornell's method**

$$D_L = 1.7 \times 10^{-9} \text{ m}^2/\text{s}$$

$$D_v = 1.45 \times 10^{-5} \text{ m}^2/\text{s}$$

$$\mu_v = 0.018 \times 10^{-3} \text{ Ns/m}^2$$

$$(Sc)_v = \frac{0.018 \times 10^{-3}}{1.21 \times 1.45 \times 10^{-5}} = 1.04$$



$$(Sc)_L = \frac{10^{-3}}{1000 \times 1.7 \times 10^{-9}} = 588$$

$$L_W^* = \frac{29.5}{1.77} = 16.7 \text{ kg/s m}^2$$

From Figure 11.41, at 60 per cent flooding,  $K_3 = 0.85$ .

From Figure 11.42, at 60 per cent flooding,  $\psi_h = 80$ .

From Figure 11.43, at  $L_W^* = 16.7$ ,  $\phi_h = 0.1$ .

$H_{OG}$  can be expected to be around 1 m, so as a first estimate  $Z$  can be taken as 8 m. The column diameter is greater than 0.6 m so the diameter correction term will be taken as 2.3.

$$\mathbf{H}_L = 0.305 \times 0.1(588)^{0.5} \times 0.85 \left( \frac{8}{3.05} \right)^{0.15} = 0.7 \text{ m} \quad (11.111)$$

As the liquid temperature has been taken as 20°C, and the liquid is water,

$$f_1 = f_2 = f_3 = 1$$

$$\mathbf{H}_G = 0.011 \times 80(1.04)^{0.5}(2.3) \left( \frac{8}{3.05} \right)^{0.33} / (16.7)^{0.5} = 0.7 \text{ m} \quad (11.110)$$

$$\mathbf{H}_{OG} = 0.7 + 0.8 \times 0.7 = 1.3 \text{ m} \quad (11.105)$$

$$Z = 8 \times 1.3 = 10.4 \text{ m, close enough to the estimated value.}$$

### ***Onda's method***

$$\mathbf{R} = 0.08314 \text{ bar m}^3/\text{kmol K.}$$

Surface tension of liquid, taken as water at 20°C =  $70 \times 10^{-3}$  N/m

$$g = 9.81 \text{ m/s}^2$$

$$d_p = 38 \times 10^{-3} \text{ m}$$

From Table 11.3, for 38 mm Intalox saddles

$$a = 194 \text{ m}^2/\text{m}^3$$

$$\sigma_c \text{ for ceramics} = 61 \times 10^{-3} \text{ N/m}$$

$$\begin{aligned} \frac{a_W}{a} &= 1 - \exp \left[ -1.45 \left( \frac{61 \times 10^{-3}}{70 \times 10^{-3}} \right)^{0.75} \left( \frac{17.6}{194 \times 10^{-3}} \right)^{0.1} \left( \frac{17.6^2 \times 194}{1000^2 \times 9.81} \right)^{-0.05} \right. \\ &\quad \left. \times \left( \frac{17.6^2}{1000 \times 70 \times 10^{-3} \times 194} \right)^{0.2} \right] = 0.71 \end{aligned} \quad (11.113)$$

$$a_W = 0.71 \times 194 = 138 \text{ m}^2/\text{m}^3$$

$$\begin{aligned} k_L \left( \frac{10^3}{10^{-3} \times 9.81} \right)^{1/3} &= 0.0051 \left( \frac{17.6}{138 \times 10^{-3}} \right)^{2/3} \left( \frac{10^{-3}}{10^3 \times 1.7 \times 10^{-9}} \right)^{-1/2} \\ &\quad \times (194 \times 38 \times 10^{-3})^{0.4} \end{aligned} \quad (11.114)$$

$$k_L = 2.5 \times 10^{-4} \text{ m/s}$$

$$V_W^* \text{ on actual column diameter} = \frac{1.39}{1.77} = 0.79 \text{ kg/m}^2\text{s}$$

$$k_G \frac{0.08314 \times 293}{194 \times 1.45 \times 10^{-5}} = 5.23 \left( \frac{0.79}{194 \times 0.018 \times 10^{-3}} \right)^{0.7} \quad (11.115)$$

$$\times \left( \frac{0.018 \times 10^{-3}}{1.21 \times 1.45 \times 10^{-5}} \right)^{1/3} (194 \times 38 \times 10^{-3})^{-2.0}$$

$$k_G = 5.0 \times 10^{-4} \text{ kmol/sm}^2 \text{ bar}$$

$$G_m = \frac{0.79}{29} = 0.027 \text{ kmol/m}^2\text{s}$$

$$L_m = \frac{16.7}{18} = 0.93 \text{ kmol/m}^2\text{s}$$

$$H_G = \frac{0.027}{5.0 \times 10^{-4} \times 138 \times 1.013} = 0.39 \text{ m} \quad (11.116)$$

$C_T$  = total concentration, as water,

$$= \frac{1000}{18} = 55.6 \text{ kmol/m}^3$$

$$H_L = \frac{0.93}{2.5 \times 10^{-4} \times 138 \times 55.6} = 0.49 \text{ m} \quad (11.117)$$

$$H_{OG} = 0.39 + 0.8 \times 0.49 = \underline{\underline{0.78 \text{ m}}} \quad (11.105)$$

Use higher value, estimated using Cornell's method, and round up packed bed height to 11 m.

### 11.14.5. Column internals

The internal fittings in a packed column are simpler than those in a plate column but must be carefully designed to ensure good performance. As a general rule, the standard fittings developed by the packing manufacturers should be specified. Some typical designs are shown in Figures 11.45 to 11.54; and their use is discussed in the following paragraphs.

#### **Packing support**

The function of the support plate is to carry the weight of the wet packing, whilst allowing free passage of the gas and liquid. These requirements conflict; a poorly designed support will give a high pressure drop and can cause local flooding. Simple grid and perforated plate supports are used, but in these designs the liquid and gas have to vie for the same openings. Wide-spaced grids are used to increase the flow area; with layers of larger size packing stacked on the grid to support the small size random packing, Figure 11.45.

The best design of packing support is one in which gas inlets are provided above the level where the liquid flows from the bed; such as the gas-injection type shown in Figure 11.46

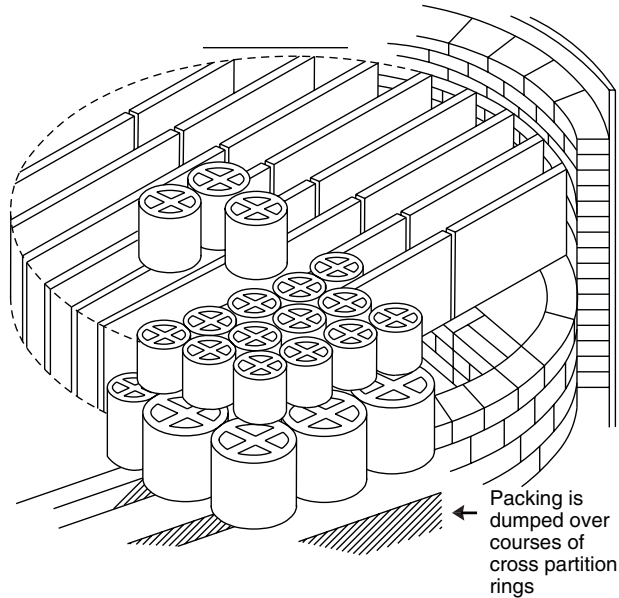


Figure 11.45. Stacked packing used to support random packing

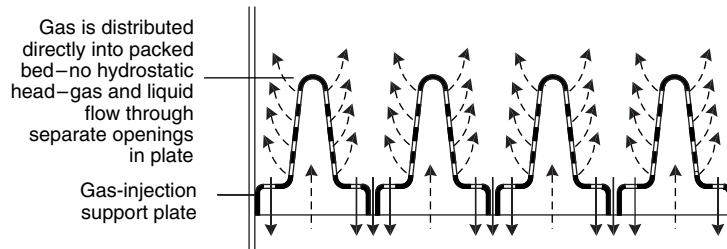


Figure 11.46. The principle of the gas-injection packing support

and 11.47. These designs have a low pressure drop and no tendency to flooding. They are available in a wide range of sizes and materials: metals, ceramics and plastics.

### **Liquid distributors**

The satisfactory performance of a plate column is dependent on maintaining a uniform flow of liquid throughout the column, and good initial liquid distribution is essential. Various designs of distributors are used. For small-diameter columns a central open feed-pipe, or one fitted with a spray nozzle, may well be adequate; but for larger columns more elaborate designs are needed to ensure good distribution at all liquid flow-rates. The two most commonly used designs are the orifice type, shown in Figure 11.48, and the weir type, shown in Figure 11.49. In the orifice type the liquid flows through holes in the plate and the gas through short stand pipes. The gas pipes should be sized to give sufficient area for gas flow without creating a significant pressure drop; the holes should be small

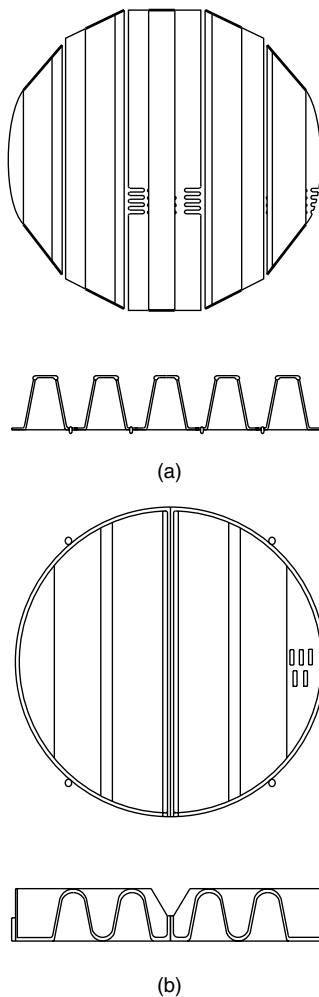


Figure 11.47. Typical designs of gas-injection supports (Norton Co.). (a) Small diameter columns (b) Large diameter columns

enough to ensure that there is a level of liquid on the plate at the lowest liquid rate, but large enough to prevent the distributor overflowing at the highest rate. In the weir type the liquid flows over notched weirs in the gas stand-pipes. This type can be designed to cope with a wider range of liquid flow rates than the simpler orifice type.

For large-diameter columns, the trough-type distributor shown in Figure 11.50 can be used, and will give good liquid distribution with a large free area for gas flow.

All distributors which rely on the gravity flow of liquid must be installed in the column level, or maldistribution of liquid will occur.

A pipe manifold distributor, Figure 11.51, can be used when the liquid is fed to the column under pressure and the flow-rate is reasonably constant. The distribution pipes and orifices should be sized to give an even flow from each element.

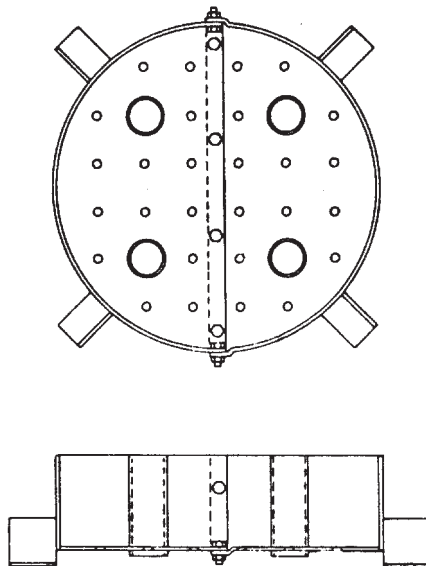


Figure 11.48. Orifice-type distributor (Norton Co.)

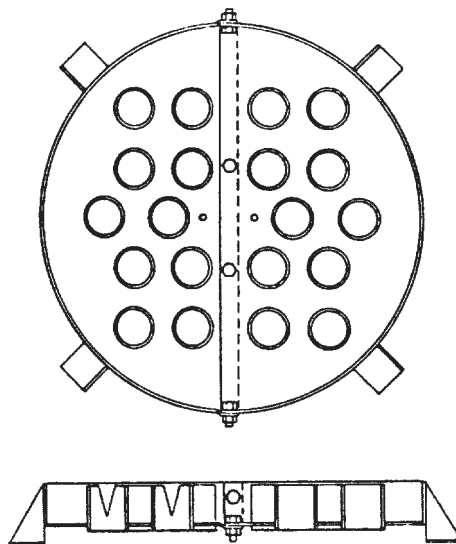


Figure 11.49. Weir-type distributor (Norton Co.)

### ***Liquid redistributors***

Redistributors are used to collect liquid that has migrated to the column walls and redistribute it evenly over the packing. They will also even out any maldistribution that has occurred within the packing.

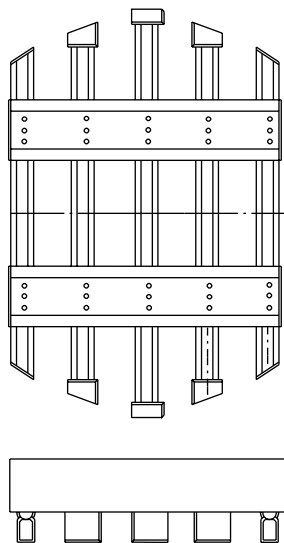


Figure 11.50. Weir-trough distributors (Norton Co.)

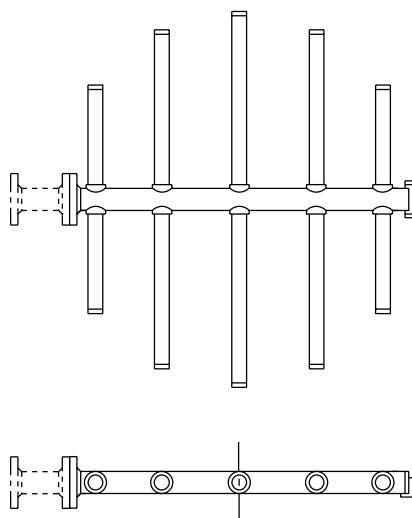


Figure 11.51. Pipe distributor (Norton Co.)

A full redistributor combines the functions of a packing support and a liquid distributor; a typical design is shown in Figure 11.52.

The “wall-wiper” type of redistributor, in which a ring collects liquid from the column wall and redirects it into the centre packing, is occasionally used in small-diameter columns, less than 0.6 m. Care should be taken when specifying this type to select a design that does not unduly restrict the gas flow and cause local flooding. A good design is that shown in Figure 11.53.

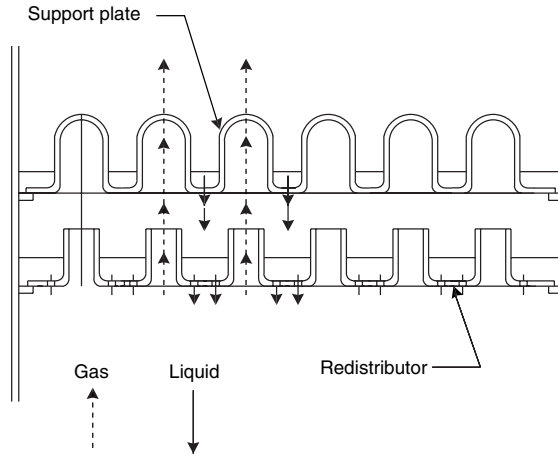


Figure 11.52. Full redistributor

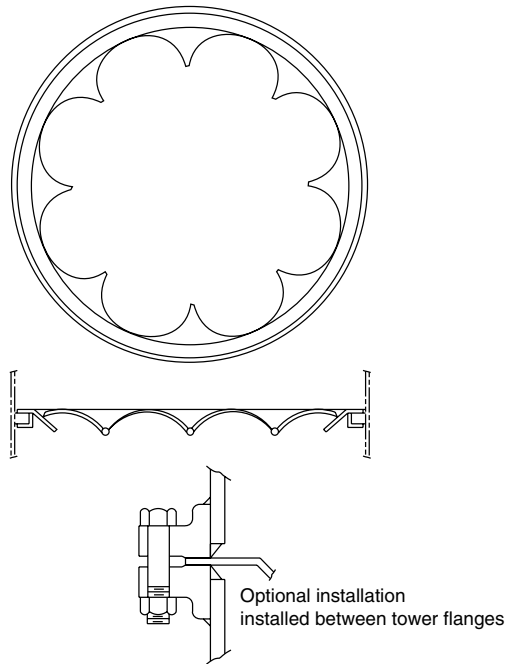


Figure 11.53. "Wall wiper" redistributor (Norton Co.)

The maximum bed height that should be used without liquid redistribution depends on the type of packing and the process. Distillation is less susceptible to maldistribution than absorption and stripping. As a general guide, the maximum bed height should not exceed 3 column diameters for Raschig rings, and 8 to 10 for Pall rings and saddles. In a large-diameter column the bed height will also be limited by the maximum weight of packing that can be supported by the packing support and column walls; this will be around 8 m.

### ***Hold-down plates***

At high gas rates, or if surging occurs through mis-operation, the top layers of packing can be fluidised. Under these conditions ceramic packing can break up and the pieces filter down the column and plug the packing; metal and plastic packing can be blown out of the column. Hold-down plates are used with ceramic packing to weigh down the top layers and prevent fluidisation; a typical design is shown in Figure 11.54. Bed-limiters are sometimes used with plastics and metal packings to prevent expansion of the bed when operating at a high-pressure drop. They are similar to hold-down plates but are of lighter construction and are fixed to the column walls. The openings in hold-down plates and bed-limiters should be small enough to retain the packing, but should not restrict the gas and liquid flow.

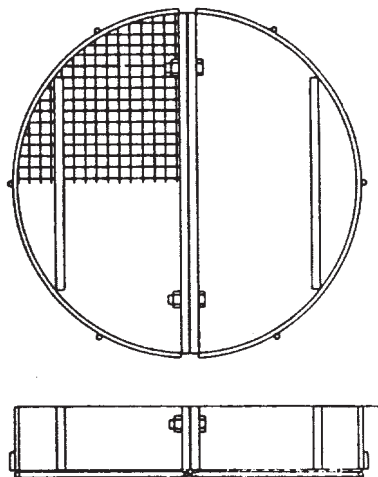


Figure 11.54. Hold-down plate design (Norton Co.)

### ***Installing packing***

Ceramic and metal packings are normally dumped into the column “wet”, to ensure a truly random distribution and prevent damage to the packing. The column is partially filled with water and the packing dumped into the water. A height of water must be kept above the packing at all times.

If the columns must be packed dry, for instance to avoid contamination of process fluids with water, the packing can be lowered into the column in buckets or other containers. Ceramic packings should not be dropped from a height of more than half a metre.

### ***Liquid hold-up***

An estimate of the amount of liquid held up in the packing under operating conditions is needed to calculate the total load carried by the packing support. The liquid hold-up will depend on the liquid rate and, to some extent, on the gas flow-rate. The packing manufacturers’ design literature should be consulted to obtain accurate estimates. As a



rough guide, a value of about 25 per cent of the packing weight can be taken for ceramic packings.

### 11.14.6. Wetting rates

If very low liquid rates have to be used, outside the range of  $F_{LV}$  given in Figure 11.44, the packing wetting rate should be checked to make sure it is above the minimum recommended by the packing manufacturer.

Wetting rate is defined as:

$$\text{wetting rate} = \frac{\text{volumetric liquid rate per unit cross-sectional area}}{\text{packing surface area per unit volume}}$$

A nomograph for the calculation of wetting rates is given in Volume 2, Chapter 4.

Wetting rates are frequently expressed in terms of mass or volume flow-rate per unit column cross-sectional area.

Kister (1992) gives values for minimum wetting rates of 0.5 to 2 gpm/ft<sup>2</sup> ( $0.35 \times 10^3$  to  $1.4 \times 10^3$  m<sup>3</sup> s<sup>-1</sup>/m<sup>2</sup>) for random packing and 0.1 to 0.2 gpm/ft<sup>2</sup> ( $0.07 \times 10^{-3}$  to  $0.14 \times 10^{-3}$  m<sup>3</sup> s<sup>-1</sup>/m<sup>2</sup>) for structured packing. Norman (1961) recommends that the liquid rate in absorbers should be kept above 2.7 kg/m<sup>2</sup>s.

If the design liquor rate is too low, the diameter of the column should be reduced. For some processes liquid can be recycled to increase the flow over the packing.

A substantial factor of safety should be applied to the calculated bed height for process where the wetting rate is likely to be low.

## 11.15. COLUMN AUXILIARIES

Intermediate storage tanks will normally be needed to smooth out fluctuations in column operation and process upsets. These tanks should be sized to give sufficient hold-up time for smooth operation and control. The hold-up time required will depend on the nature of the process and on how critical the operation is; some typical values for distillation processes are given below:

<i>Operation</i>	<i>Time, minutes</i>
Feed to a train of columns	10 to 20
Between columns	5 to 10
Feed to a column from storage	2 to 5
Reflux drum	5 to 15

The time given is that for the level in the tank to fall from the normal operating level to the minimum operating level if the feed ceases.

Horizontal or vertical tanks are used, depending on the size and duty. Where only a small hold-up volume is required this can be provided by extending the column base, or, for reflux accumulators, by extending the bottom header of the condenser.

The specification and sizing of surge tanks and accumulators is discussed in more detail by Mehra (1979) and Evans (1980).

## 11.16. SOLVENT EXTRACTION (LIQUID-LIQUID EXTRACTION)

Extraction should be considered as an alternative to distillation in the following situations:

1. Where the components in the feed have close boiling points. Extraction in a suitable solvent may be more economic if the relative volatility is below 1.2.
2. If the feed components form an azeotrope.
3. If the solute is heat sensitive, and can be extracted in to a lower boiling solvent, to reduce the heat history during recovery.

### ***Solvent selection***

The following factors need to be considered when selecting a suitable solvent for a given extraction.

1. Affinity for solute: the selectivity, which is a measure of the distribution of the solute between the two solvents (concentration of solute in feed-solvent divided by the concentration in extraction-solvent). Selectivity is analogous to relative volatility in distillation. The greater the difference in solubility of the solute between the two solvents, the easier it will be to extract.
2. Partition ratio: this is the weight fraction of the solute in the extract divided by the weight fraction in the raffinate. This determines the quantity of solvent needed. The less solvent needed the lower will be the solvent and solvent recovery costs.
3. Density: the greater the density difference between the feed and extraction solvents the easier it will be to separate the solvents.
4. Miscibility: ideally the two solvents should be immiscible. The greater the solubility of the exaction solvent in the feed solvent the more difficult it will be to recover the solvent from the raffinate, and the higher the cost.
5. Safety: if possible, and all other factors considered, a solvent should be chosen that is not toxic nor dangerously inflammable.
6. Cost: the purchase cost of the solvent is important but should not be considered in isolation from the total process costs. It may be worth considering a more expensive solvent if it is more effective and easier to recover.

### 11.16.1. Extraction equipment

Extraction equipment can be divided into two broad groups:

1. Stage-wise extractors, in which the liquids are alternately contacted (mixed) and then separated, in a series of stages. The “mixer-settler” contactor, is an example of this type. Several mixer-settlers are often used in series to increase the effectiveness of the extraction.
2. Differential extractors, in which the phases are continuously in contact in the extractor and are only separated at the exits; for example, in packed column extractors.

Extraction columns can be further sub-divided according to the method used to promote contact between the phases: packed, plate, mechanically agitated, or pulsed columns. Various types of proprietary centrifugal extractors are also used.

The following factors need to be taken into consideration when selecting an extractor for a particular application:

1. The number of stages required.
2. The throughputs.
3. The settling characteristics of the phases.
4. The available floor area and head room.

Hanson (1968) has given a selection guide based on these factors, which can be used to select the type of equipment most likely to be suitable, Figure 11.55.

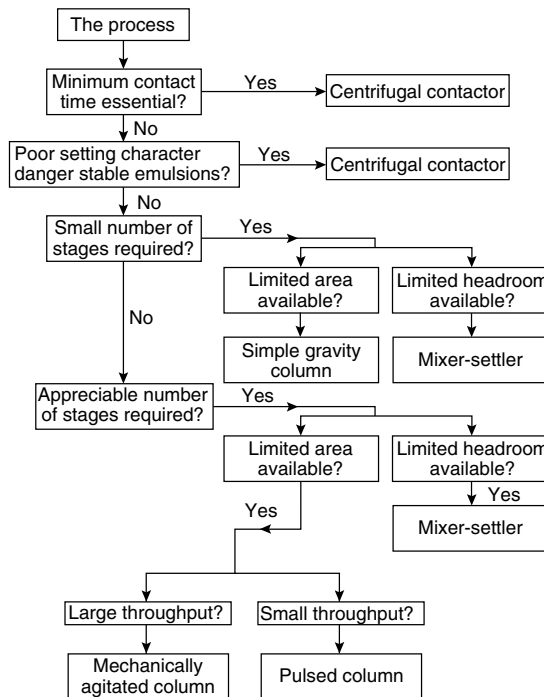


Figure 11.55. Selection guide for liquid–liquid contactors (after Hanson, 1968)

The fields of application of the various types of extraction equipment are also well summarised in Volume 2, Chapter 13. The basic principles of liquid–liquid extraction are covered in several specialist texts: Treybal (1980), Robbins (1997), and Humphrey and Keller (1997).

### 11.16.2. Extractor design

#### *Number of stages*

The primary task in the design of an extractor for a liquid–liquid extraction process is the determination of the number of stages needed to achieve the separation required.

The stages may be arranged in three ways:

1. Fresh solvent fed to each stage, the raffinate passing from stage to stage.
2. The extracting solvent fed co-currently with the raffinate, from stage to stage.
3. The extracting solvent fed counter-current to the raffinate.

Counter-current flow is the most efficient method and the most commonly used. It will give the greatest concentration of the solute in the extract, and the least use of solvent.

### **Equilibrium data**

To determine the number of stages it best to plot the equilibrium data on a triangular diagram, Figure 11.56. Each corner of the triangle represents 100% of the feed-solvent, solute or extraction-solvent. Each side shows the composition of one of the binary pairs. The ternary compositions are shown in the interior of the triangular. Mixtures within the region bounded by the curve will separate into two phases. The tie-lines link the equilibrium compositions of the separate phases. The tie-lines reduce in length toward the top of the curve. The point where they disappear is called the *plait* point.

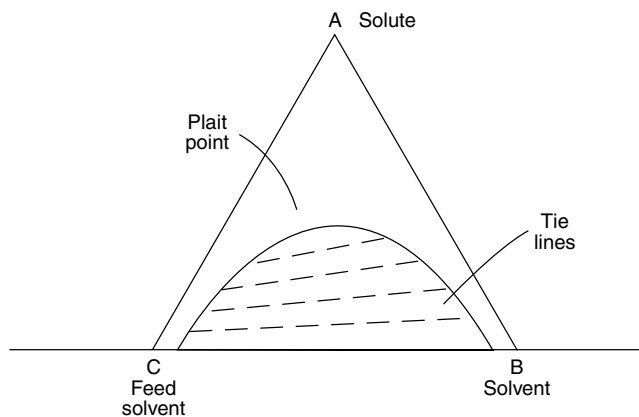


Figure 11.56. Equilibrium diagram solute distributed between two solvents

A fuller discussion of the various classes of diagram used to represent liquid–liquid equilibria is given in Volume 2, Chapter 13; see also Treybal (1980) and Humphrey *et al.* (1984).

The most comprehensive source of equilibrium data for liquid–liquid systems is the DECHEMA data series, Sorensen and Arlt (1979). Equilibrium data for some systems is also given by Perry *et al.* (1997).

The UNIQUAC and UNIFAC equations can be used to estimate liquid–liquid equilibria, see Chapter 8.

### **Number of stages**

The number of stages required for a given separation can be determined from the triangular diagram using a method analogous to the McCabe–Thiele diagram used to determine the

number of theoretical stages (plates) in distillation. The method set out below is for counter-current extraction.

### Procedure

Refer to Figures 11.56 and 11.57.

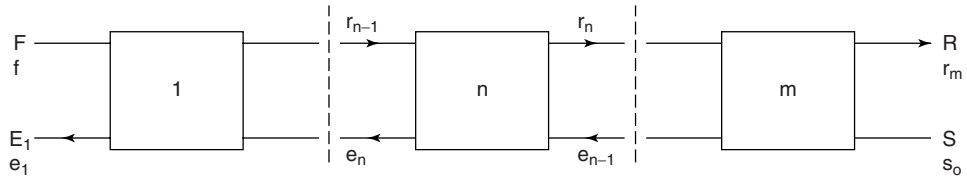


Figure 11.57. Counter-current extraction

Let the flow-rates be:

$F$  = feed, of the solution to be extracted  
 $E$  = extract  
 $R$  = raffinate  
 $S$  = the extracting solvent

and the compositions:

$r$  = raffinate  
 $e$  = extract  
 $s$  = solvent  
 $f$  = feed

Then a material balance over stage  $n$  gives:

$$F + E_{n+1} = R_n + E_1$$

It can be shown that the difference in flow-rate between the raffinate leaving any stage,  $R_n$ , and the extract entering the stage,  $E_n$ , is constant. Also, that the difference between the amounts of each component entering and leaving a stage is constant. This means that if lines are drawn on the triangular diagram linking the composition of the raffinate from a stage and the extract entering from the next stage, they will pass through a common pole when extrapolated. The number of stages needed can be found by making use of this construction and the equilibrium compositions given by the tie-lines.

### Construction

1. Draw the liquid-liquid equilibrium data on triangular graph paper. Show sufficient tie-lines to enable the equilibrium compositions to be determined at each stage.
2. Mark the feed and extraction-solvent compositions on the diagram. Join them with a line. The composition of a mixture of the feed and solvent will lie on this line.
3. Calculate the composition of the mixture given by mixing the feed with the extraction solvent. Mark this point, 0, on the line drawn in step 2.

4. Mark the final raffinate composition,  $r_m$  on the equilibrium curve.
5. Draw a line from  $r_m$  through the point 0. This will cut the curve at the final extract composition,  $e_1$ .  
Note: if the extract composition is specified, rather than the raffinate, draw the line from  $e_1$  through 0 to find  $r_m$ .
6. Draw a line from the solvent composition,  $S_0$  through  $r_m$  and extend it beyond  $r_m$ .
7. Draw a line from  $e_1$  through  $f$  and extend it to cross the line drawn in step 6, at the pole point,  $P$ .
8. Find the composition of the raffinate leaving the first stage,  $r_1$  by judging the position of the tie-line from  $e_1$ . Draw a line from the pole point,  $P$ , through  $r_1$  to cut the curve at  $e_2$ , the extract leaving stage 2.
9. Repeat this procedure until sufficient stages have been drawn to reach the desired raffinate final composition.

If an extended tie-line passes through the pole point  $P$ , an infinite number of stages will be needed. This condition sets the minimum flow of extraction-solvent required. It is analogous to a pinch point in distillation.

The method is illustrated in Example 11.15.

### Example 11.15

Acetone is to be extracted from a solution in water, using 1,1,2-trichloroethane. The feed concentration is 45.0 per cent w/w acetone. Determine the number of stages required to reduce the concentration of acetone to below 10 per cent, using 32 kg of extraction-solvent per 100 kg feed.

The equilibrium data for this system are given by Treybal *et al. Ind. Eng. Chem.* **38**, 817 (1946).

### Solution

Composition of feed + solvent, point  $o = 0.45 \times 100 / (100 + 32) = 0.34 = 34$  per cent. Draw line from TCE (trichloroethane) = 100 per cent, point  $s_0$ , to feed composition,  $f$ , 45 per cent acetone.

Mark point  $o$  on this line at 34 per cent acetone.

Mark required final raffinate composition,  $r_m$ , on the equilibrium curve, at 10 per cent.

Draw line from this point through point  $o$  to find final extract composition,  $e_1$ .

Draw line from this point through the feed composition,  $f$ , extend this line to cut a line extended from  $s_0$  through  $r_m$ , at  $P$ .

Using the tie-lines plotted on the figure, judge the position that a tie-line would have from  $e_1$  and mark it in, to find the point on the curve giving the composition of the raffinate leaving the first stage,  $r_1$ .

Draw a line through from the pole point  $P$  through  $r_1$ , to find the point on the curve giving the extract composition leaving the second stage,  $e_2$ .

Repeat these steps until the raffinate composition found is below 10 per cent.

From the diagram, Figure 11.58, it can be seen that five stages are needed.

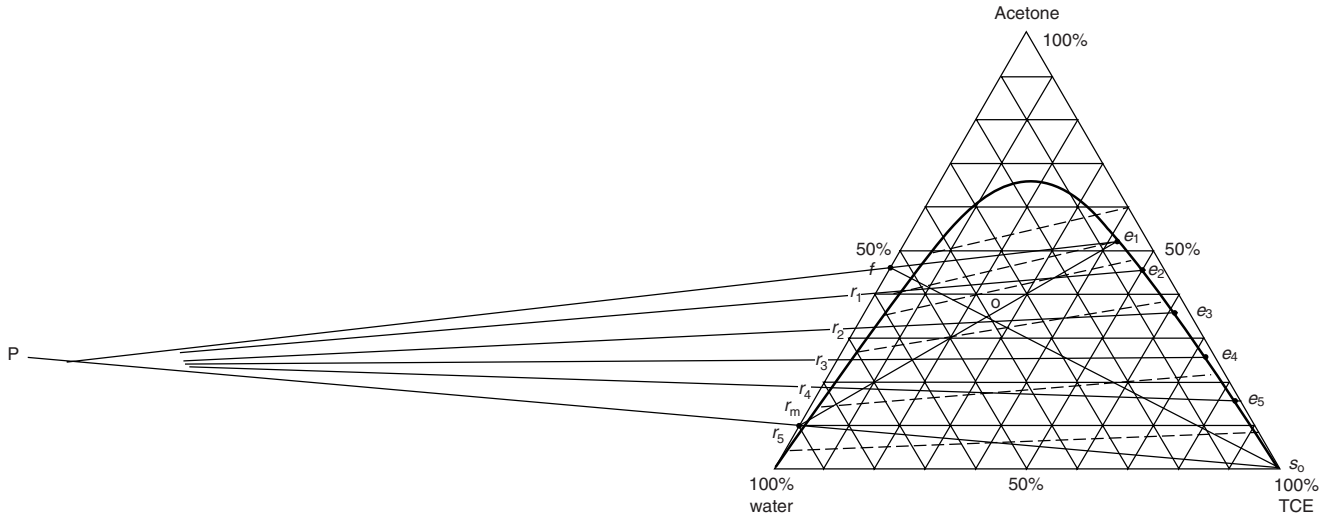


Figure 11.58. Example 11.15

That the raffinate composition from stage 5 passes through the specified raffinate composition of 10 per cent is fortuitous. As the construction, particularly the judgement of the position of the tie-lines, is approximate, the number of stages will be increased to six. This should ensure that the specified raffinate composition of below 10 per cent is met.

### ***Immiscible solvents***

If the solvents are immiscible the procedure for determining the number of stages required is simplified. The equilibrium curve can be drawn on regular, orthogonal, graph paper. An operating line, giving the relationship between the compositions of the raffinate and extracts entering and leaving each stage, can then be drawn, and the stages stepped off. The procedure is similar to the McCabe–Thiele construction for determining the number of stages in distillation; Section 11.5.2. The slope of the operating line is the ratio of the final raffinate to fresh solvent flow-rates.

For a full discussion of the methods that can be used to determine the stage requirements in liquid–liquid extraction refer to Treybal (1980), Perry *et al.* (1997) and Robbins (1997).

Computer programs are available for the design of extraction processes and would normally be included in the various commercial process simulation packages available; see Chapter 4.

### **11.16.3. Extraction columns**

The simplest form of extractor is a spray column. The column is empty; one liquid forms a continuous phase and the other liquid flows up, or down, the column in the form of droplets. Mass transfer takes place to, or from, the droplets to the continuous phase. The efficiency of a spray tower will be low, particularly with large diameter columns, due to back mixing. The efficiency of the basic, empty, spray column can be improved by installing plates or packing.

Sieve plates are used, similar to those used for distillation and absorption. The stage efficiency for sieve plates, expressed in terms the height of an equivalent theoretical stage (HETS), will, typically, range from 1 to 2.5 m.

Random packings are also used; they are the same as those used in packed distillation and absorption columns. The properties of random packings are given in Table 11.3. Proprietary structured packing are also used.

Mass transfer in packed columns is a continuous, differential, process, so the transfer unit method should be used to determine the column height, as used in absorption; see Section 11.14.2. However, it is often convenient to treat them as staged processes and use the HETS for the packing employed. For random packings the HETS will, typically, range from 0.5 to 1.5 m, depending on the type and size of packing used.

### ***Flooding***

No simple correlation is available to predict the flooding velocities in extraction columns, and hence the column diameter needed. The more specialised texts should be consulted to obtain guidance on the appropriate method to use for a particular problem; see Treybal (1980), Perry *et al.* (1997) and Humphrey and Keller (1997).



### 11.16.4. Supercritical fluid extraction

A recent development in liquid–liquid extraction has been the use of supercritical fluids as the extraction-solvent. Carbon dioxide at high pressure is the most commonly used fluid. It is used in processes for the decaffeination of coffee and tea. The solvent can be recovered from the extract solution as a gas, by reducing the pressure. Super critical extraction processes are discussed by Humphrey and Keller (1997).

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## 11.18. NOMENCLATURE

		Dimensions in $MLT\theta$
$A$	Constant in equation 11.63	—
$A_a$	Active area of plate	$L^2$
$A_{ap}$	Clearance area under apron	$L^2$
$A_c$	Total column cross-sectional area	$L^2$
$A_d$	Downcomer cross-sectional area	$L^2$
$A_h$	Total hole area	$L^2$
$A_i$	Absorption factor	—
$A_m$	Area term in equation 11.92	$L^2$
$A_n$	Net area available for vapour-liquid disengagement	$L^2$
$A_p$	Perforated area	$L^2$
$a$	Packing surface area per unit volume	$L^{-1}$
$a_w$	Effective interfacial area of packing per unit volume	$L^{-1}$
$B$	Mols of bottom product per unit time	$MT^{-1}$
$b$	Parameter in equation 11.28	—
$b_i$	Mols of component $i$ in bottom product	$M$
$C_o$	Orifice coefficient in equation 11.88	—
$C_T$	Total molar concentration	$ML^{-3}$
$c$	Parameter defined by equation 11.32	—
$D$	Mols of distillate per unit time	$MT^{-1}$
$D_c$	Column diameter	$L$
$D_e$	Eddy diffusivity	$L^2T^{-1}$
$D_L$	Liquid diffusivity	$L^2T^{-1}$
$D_{LK}$	Diffusivity of light key component	$L^2T^{-1}$
$D_v$	Diffusivity of vapour	$L^2T^{-1}$
$d_h$	Hole diameter	$L$
$d_i$	Mols of component $i$ in distillate per unit time	$MT^{-1}$
$d_p$	Size of packing	$L$
$E$	Extract flow-rate	$MT^{-1}$
$E_a$	Actual plate efficiency, allowing for entrainment	—
$E_{mV}$	Murphree plate efficiency	—
$E_{mv}$	Murphree point efficiency	—
$E_o$	Overall column efficiency	—
$e$	Extract composition	—
FA	Fractional area, equation 11.69	—
$F$	Feed, of the solution to be extracted	$MT^{-1}$
$F_n$	Feed rate to stage $n$	$MT^{-1}$
$F_p$	Packing factor	$L^{-1}$
$F_v$	Column 'F' factor = $u_a\sqrt{\rho_v}$	$M^{1/2}L^{-1/2}T^{-1}$
$F_{LV}$	Column liquid-vapour factor in Figure 11.27	—
$f$	Feed composition	—
$f_i$	Mols of component $i$ in feed per unit time	$MT^{-1}$
$f_1$	Viscosity correction factor in equation 11.110	—
$f_2$	Liquid density correction factor in equation 11.110	—
$f_3$	Surface tension correction factor in equation 11.110	—
$G$	Feed condition factor defined by equations 11.55 and 11.56	—
$G_m$	Molar flow-rate of gas per unit area	$ML^{-2}T^{-1}$
$g$	Gravitational acceleration	$LT^{-2}$
$H$	Specific enthalpy of vapour phase	$L^2T^{-2}$
$H_G$	Height of gas film transfer unit	$L$
$H_L$	Height of liquid film transfer unit	$L$
$H_{OG}$	Height of overall gas phase transfer unit	$L$
$H_{OL}$	Height of overall liquid phase transfer unit	$L$
$\mathcal{H}$	Henry's constant	$ML^{-1}T^{-2}$

$h$	Specific enthalpy of liquid phase	$L^2T^{-2}$
$h_{ap}$	Apron clearance	L
$h_b$	Height of liquid backed-up in downcomer	L
$h_{bc}$	Downcomer back-up in terms of clear liquid head	L
$h_d$	Dry plate pressure drop, head of liquid	L
$h_{dc}$	Head loss in downcomer	L
$h_f$	Specific enthalpy of feed stream	$L^2T^{-2}$
$h_{ow}$	Height of liquid crest over downcomer weir	L
$h_r$	Plate residual pressure drop, head of liquid	L
$h_t$	Total plate pressure drop, head of liquid	L
$h_w$	Weir height	L
$K$	Equilibrium constant for least volatile component	—
$K'$	Equilibrium constant for more volatile component	—
$K_G$	Overall gas phase mass transfer coefficient	$L^{-1}T$
$K_i$	Equilibrium constant for component $i$	—
$K_L$	Overall liquid phase mass transfer coefficient	$LT^{-1}$
$K_n$	Equilibrium constant on stage $n$	—
$K_1$	Constant in equation 11.81	$LT^{-1}$
$K_2$	Constant in equation 11.84	—
$K_3$	Percentage flooding factor in equation 11.111	—
$K_4$	Parameter in Fig. 11.44, defined by equation 11.118	—
$K_5$	Constant in equation 11.115	—
$k$	Root of equation 11.28	—
$k_G$	Gas film mass transfer coefficient	$L^{-1}T$
$k_L$	Liquid film mass transfer coefficient	$LT^{-1}$
$L$	Liquid flow-rate, mols per unit time	$MT^{-1}$
$L_e$	Estimated flow-rate of combined keys, liquid	$MT^{-1}$
$L_m$	Molar flow-rate of liquid per unit area	$ML^{-2}T^{-1}$
$L_p$	Volumetric flow-rate across plate divided by average plate width	$L^2T^{-1}$
$L_w$	Liquid mass flow-rate	$MT^{-1}$
$L_w^*$	Liquid mass flow-rate per unit area	$MT^{-2}T^{-1}$
$L_{wd}$	Liquid mass flow-rate through downcomer	$MT^{-1}$
$\underline{l}_i$	Limiting liquid flow-rate of components lighter than the keys in the rectifying section	$MT^{-1}$
$\underline{l}'_i$	Limiting liquid flow-rates of components heavier than the keys in the stripping section	$MT^{-1}$
$l_h$	Weir chord height	L
$l_n$	Molar liquid flow rate of component from stage $n$	$MT^{-1}$
$l_p$	Pitch of holes (distance between centres)	L
$l_t$	Plate spacing in column	L
$l_w$	Weir length	L
$M_s$	Molecular weight of solvent	—
$m$	Slope of equilibrium line	—
$N$	Number of stages	—
$N_G$	Number of gas-film transfer units	—
$N_L$	Number of liquid-film transfer units	—
$N_m$	Number of stages at total reflux	—
$N_{OG}$	Number of overall gas-phase transfer units	—
$N_{OL}$	Number of overall liquid-phase transfer units	—
$N_r$	Number of equilibrium stages above feed	—
$N_r^*$	Number of stages in rectifying section (equation 11.26)	—
$N_s$	Number of equilibrium stages below feed	—
$N_s^*$	Number of stages in stripping section (equation 11.25)	—
$n$	Stage number	—
$P$	Total pressure	$ML^{-1}T^{-2}$
$P^o$	Vapour pressure	$ML^{-1}T^{-2}$

$\Delta P_t$	Total plate pressure drop	$ML^{-1}T^{-2}$
$p$	Partial pressure	$ML^{-1}T^{-2}$
$q$	Heat to vaporise one mol of feed divided by molar latent heat	—
$q_b$	Heat supplied to reboiler	$ML^2T^{-3}$
$q_c$	Heat removed in condenser	$ML^2T^{-3}$
$q_n$	Heat supplied to or removed from stage $n$	$ML^2T^{-3}$
$R$	Universal gas constant	$L^2T^{-2}\theta^{-1}$
$R$	Reflux ratio	—
$R$	Raffinate flow-rate	$MT^{-1}$
$R_m$	Minimum reflux ratio	—
$r$	Raffinate composition	—
$S$	Extracting solvent flow-rate	$MT^{-1}$
$S_i$	Stripping factor	—
$S_n$	Side stream flow from stage $n$	$MT^{-1}$
$S_r$	Stripping factor for rectifying section (equation 11.54)	—
$S_s$	Stripping factor for stripping section (equation 11.54)	—
$s$	Slope of operating line	—
$s$	Solvent composition	—
$t_L$	Liquid contact time	$T$
$t_r$	Residence time in downcomer	$T$
$u_a$	Vapour velocity based on active area	$LT^{-1}$
$u_f$	Vapour velocity at flooding point	$LT^{-1}$
$u_h$	Vapour velocity through holes	$LT^{-1}$
$u_n$	Vapour velocity based on net cross-sectional area	$LT^{-1}$
$u_v$	Superficial vapour velocity (based on total cross-sectional area)	$LT^{-1}$
$V$	Vapour flow-rate mols per unit time	$MT^{-1}$
$V_e$	Estimated flow-rate of combined keys, vapour	$MT^{-1}$
$V_w$	Vapour mass flow-rate	$MT^{-1}$
$V_w^*$	Vapour mass flow-rate per unit area	$ML^{-2}T^{-1}$
$\underline{v}_i$	Limiting vapour flow-rates of components lighter than the keys in the rectifying section	$MT^{-1}$
$\underline{v}'_i$	Limiting vapour flow-rates of components heavier than the keys in the stripping section	$MT^{-1}$
$v_n$	Molar vapour flow-rate of component from stage $n$	$MT^{-1}$
$x$	Mol fraction of component in liquid phase	—
$x_A$	Mol fraction of component A in binary mixture	—
$x_B$	Mol fraction of component B in binary mixture	—
$x_b$	Mol fraction of component in bottom product	—
$x_d$	Mol fraction of component in distillate	—
$x_e$	Equilibrium concentration	—
$x_i$	Mol fraction of component $i$	—
$x_r$	Concentration of reference component (equation 11.57)	—
$x_n^*$	Reference concentration in equation 11.30	—
$x_o^*$	Reference concentration in equation 11.30	—
$x_1$	Concentration of solute in solution at column base	—
$x_2$	Concentration of solute in solution at column top	—
$x_r$	Reference concentration equations 11.25 and 11.26	—
$y$	Mol fraction of component in vapour phase	—
$y_A$	Mol fraction of component A in a binary mixture	—
$y_B$	Mol fraction of component B in a binary mixture	—
$y_e$	Equilibrium concentration	—
$y_i$	Mol fraction of component $i$	—
$\Delta y$	Concentration driving force in the gas phase	—
$\Delta y_{lm}$	Log mean concentration driving force	—
$y_1$	Concentration of solute in gas phase at column base	—
$y_2$	Concentration of solute in gas phase at column top	—
$Z$	Height of packing	$L$

$Z_c$	Liquid hold-up on plate	<b>L</b>
$Z_L$	Length of liquid path	<b>L</b>
$z_i$	Mol fraction of component $i$ in feed stream	—
$z_f$	Mol fraction of component in feed stream	—
$z_f^*$	Pseudo feed concentration defined by equation 11.41	—
$\alpha$	Relative volatility	—
$\alpha_i$	Relative volatility of component $i$	—
$\alpha_a$	Average relative volatility of light key	—
$\beta$	Parameter defined by equation 11.31	—
$\theta$	Root of equation 11.61	—
$\mu$	Dynamic viscosity	<b>ML<sup>-1</sup>T<sup>-1</sup></b>
$\mu_a$	Molar average liquid viscosity	<b>ML<sup>-1</sup>T<sup>-1</sup></b>
$\mu_s$	Viscosity of solvent	<b>ML<sup>-1</sup>T<sup>-1</sup></b>
$\mu_w$	Viscosity of water at 20°C	<b>ML<sup>-1</sup>T<sup>-1</sup></b>
$\rho$	Density	<b>ML<sup>-3</sup></b>
$\rho_w$	Density of water at 20°C	<b>ML<sup>-3</sup></b>
$\sigma$	Surface tension	<b>MT<sup>-2</sup></b>
$\sigma_c$	Critical surface tension for packing material	<b>MT<sup>-2</sup></b>
$\sigma_w$	Surface tension of water at 20°C	<b>MT<sup>-2</sup></b>
$\Phi$	Intercept of operating line on $Y$ axis	—
$\Phi_n$	Factor in equation 11.43	—
$\psi$	Fractional entrainment	—
$\psi_n$	Factor in equation 11.42	—
Dg	Surface tension number	
Pe	Peclet number	
Re	Reynolds number	
Sc	Schmidt number	
<i>Suffixes</i>		
$L$	Liquid	
$v$	Vapour	
HK	Heavy key	
LK	Light key	
$b$	Bottoms	
$d$	Distillate (Tops)	
$f$	Feed	
$i$	Component number	
$n$	Stage number	
1	Base of packed column	
2	Top of packed column	
<i>Superscripts</i>		
'	Stripping section of column	
<i>Subscripts</i>		
$m$	Last stage	
$n$	Stage number	

## 11.19. PROBLEMS

- 11.1.** At a pressure of 10 bar, determine the bubble and dew point of a mixture of hydrocarbons, composition, mol per cent: n-butane 21, n-pentane 48, n-hexane 31. The equilibrium  $K$  factors can be estimated using the De Priester charts in Chapter 8.
- 11.2.** The feed to a distillation column has the following composition, mol per cent: propane 5.0, isobutane 15, n-butane 25, isopentane 20, n-pentane 35. The feed is

preheated to a temperature of  $90^{\circ}\text{C}$ , at 8.3 bar pressure. Estimate the proportion of the feed which is vapour.

The equilibrium K factors are given in Example 11.9.

- 11.3.** Propane is separated from propylene by distillation. The compounds have close boiling points and the relative volatility will be low. For a feed composition of 10 per cent w/w propane, 90 per cent w/w propylene, estimate the number of theoretical plates needed to produce propylene overhead with a minimum purity of 99.5 mol per cent. The column will operate with a reflux ratio of 20. The feed will be at its boiling point. Take the relative volatility as constant at 1.1.
- 11.4.** The composition of the feed to a debutaniser is given below. Make a preliminary design for a column to recover 98 per cent of the n-butane overhead and 95 per cent of the isopentane from the column base. The column will operate at 14 bar and the feed will be at its boiling point. Use the short-cut methods and follow the procedure set out below. Use the De Priester charts to determine the relative volatility. The liquid viscosity can be estimated using the data given in Appendix D.
- Investigate the effect of reflux ratio on the number of theoretical stages.
  - Select the optimum reflux ratio.
  - Determine the number of stages at this reflux ratio.
  - Estimate the stage efficiency.
  - Determine the number of real stages.
  - Estimate the feed point.
  - Estimate the column diameter.

Feed composition:

		kg/h
propane	$\text{C}_3$	910
isobutane	i- $\text{C}_4$	180
n-butane	n- $\text{C}_4$	270
isopentane	i- $\text{C}_5$	70
normal pentane	n- $\text{C}_5$	90
normal hexane	n- $\text{C}_6$	20

- 11.5.** In a process for the manufacture of acetone, acetone is separated from acetic acid by distillation. The feed to the column is 60 mol per cent acetone, the balance acetic acid.
- The column is to recover 95 per cent of the acetone in the feed with a purity of 99.5 mol per cent acetone. The column will operate at a pressure of 760 mmHg and the feed will be preheated to  $70^{\circ}\text{C}$ .
- For this separation, determine:
- the number of minimum number of stages required,
  - the minimum reflux ratio,
  - the number of theoretical stages for a reflux ratio 1.5 times the minimum,
  - the number of actual stages if the plate efficiency can be taken as 60 per cent.



Equilibrium data for the system acetone–acetic acid, at 760 mmHg, mol fractions acetone:

liquid										
phase	0.10	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
vapour										
phase	0.31	0.56	0.73	0.84	0.91	0.95	0.97	0.98	0.99	
boiling										
point °C	103.8	93.1	85.8	79.7	74.6	70.2	66.1	62.6	59.2	

Reference: Othmer, D. F. *Ind. Eng. Chem.* **35**, 614 (1943).

- 11.6.** In the manufacture of absolute alcohol by fermentation, the product is separated and purified using several stages of distillation. In the first stage, a mixture of 5 mol per cent ethanol in water, with traces of acetaldehyde and fusel oil, is concentrated to 50 mol per cent. The concentration of alcohol in the wastewater is reduced to less than 0.1 mol per cent.

Design a sieve plate column to perform this separation, for a feed rate of 10,000 kg/hour. Treat the feed as a binary mixture of ethanol and water.

Take the feed temperature as 20 °C. The column will operate at 1 atmosphere.

Determine:

- the number of theoretical stages,
- an estimate of the stage efficiency,
- the number of actual stages needed.

Design a suitable sieve plate for conditions below the feed point.

Equilibrium data for the system ethanol–water, at 760 mmHg, mol fractions ethanol:

liquid										
phase	0.019	0.072	0.124	0.234	0.327	0.508	0.573	0.676	0.747	0.894
vapour										
phase	0.170	0.389	0.470	0.545	0.583	0.656	0.684	0.739	0.782	0.894
boiling										
point										
°C	95.5	89.0	85.3	82.7	81.5	79.8	79.3	78.7	78.4	78.2

Reference: Carey, J. S. and Lewis, W. K. *Ind. Eng. Chem.* **24**, 882 (1932).

- 11.7.** In the manufacture of methyl ethyl ketone from butanol, the product is separated from unreacted butanol by distillation. The feed to the column consists of a mixture of 0.90 mol fraction MEK, 0.10 mol fraction 2-butanol, with a trace of trichloroethane.

The feed rate to the column is 20 kmol/h and the feed temperature 35 °C. The specifications required are: top product 0.99 mol fraction MEK; bottom product 0.99 mol fraction butanol.

Design a column for this separation. The column will operate at essentially atmospheric pressure. Use a reflux ratio 1.5 times the minimum.

- determine the minimum reflux ratio,
- determine the number of theoretical stages,

- (c) estimate the stage efficiency,
- (d) determine the number of actual stages needed,
- (e) design a suitable sieve plate for conditions below the feed point.

Equilibrium data for the system MEK–2-butanol, mol fractions MEK:

liquid									
phase	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
vapour									
phase	0.23	0.41	0.53	0.64	0.73	0.80	0.86	0.91	0.95
boiling									
point °C	97	94	92	90	87	85	84	82	80

- 11.8.** A column is required to recover acetone from an aqueous solution. The feed contains 5 mol per cent acetone. A product purity of 99.5 per cent w/w is required and the effluent water must contain less than 100 ppm acetone. The feed temperature will range from 10 to 25 °C. The column will operate at atmospheric pressure. For a feed of 7500 kg/h, compare the designs for a sieve plate and packed column, for this duty. Use a reflux ratio of 3. Compare the capital and utility cost for the two designs. No reboiler is required for this column; live steam can be used. Equilibrium data for the system acetone–water is given in Example 11.2.

- 11.9.** In the manufacture of methyl ethyl ketone (MEK), the product MEK is extracted from a solution in water using 1,1,2 trichloroethane as the solvent. For a feed rate 2000 kg/h of solution, composition 30 per cent w/w MEK, determine the number of stages required to recover 95 per cent of the dissolved MEK; using 700 kg/h TCE, with counter-current flow. Tie-line data for the system MEK–water–TCE percentages w/w, from Newman *et al.*, *Ind. Eng. Chem.* **41**, 2039 (1949).

water-rich phase		solvent-rich phase	
MEK	TCE	MEK	TCE
18.15	0.11	75.00	19.92
12.78	0.16	58.62	38.65
9.23	0.23	44.38	54.14
6.00	0.30	31.20	67.80
2.83	0.37	16.90	82.58
1.02	0.41	5.58	94.42

- 11.10.** Chlorine is to be removed from a vent stream by scrubbing with a 5 per cent w/w aqueous solution of sodium hydroxide. The vent stream is essential nitrogen, with a maximum concentration of 5.5 per cent w/w chlorine. The concentration of chlorine leaving the scrubber must be less than 50 ppm by weight. The maximum flow-rate of the vent stream to the scrubber will be 4500 kg/h. Design a suitable packed column for this duty. The column will operate at 1.1 bar and ambient temperature. If necessary, the aqueous stream may be recirculated to maintain a suitable wetting rate. Note: the reaction of chlorine with the aqueous solution will be rapid and there will be essentially no back-pressure of chlorine from the solution.

# *Heat-transfer Equipment*

## 12.1. INTRODUCTION

The transfer of heat to and from process fluids is an essential part of most chemical processes. The most commonly used type of heat-transfer equipment is the ubiquitous shell and tube heat exchanger; the design of which is the main subject of this chapter.

The fundamentals of heat-transfer theory are covered in Volume 1, Chapter 9; and in many other textbooks: Holman (2002), Ozisik (1985), Rohsenow *et al.* (1998), Kreith and Bohn (2000), and Incropera and Dewitt (2001).

Several useful books have been published on the design of heat exchange equipment. These should be consulted for fuller details of the construction of equipment and design methods than can be given in this book. A selection of the more useful texts is listed in the bibliography at the end of this chapter. The compilation edited by Schlünder (1983ff), see also the edition by Hewitt (1990), is probably the most comprehensive work on heat exchanger design methods available in the open literature. The book by Saunders (1988) is recommended as a good source of information on heat exchanger design, especially for shell-and-tube exchangers.

As with distillation, work on the development of reliable design methods for heat exchangers has been dominated in recent years by commercial research organisations: Heat Transfer Research Inc. (HTRI) in the United States and Heat Transfer and Fluid Flow Service (HTFS) in the United Kingdom. HTFS was developed by the United Kingdom Atomic Energy Authority and the National Physical Laboratory, but is now available from AspenTech, see Chapter 4, Table 4.1. Their methods are of a proprietary nature and are not therefore available in the open literature. They will, however, be available to design engineers in the major operating and contracting companies, whose companies subscribe to these organisations.

The principal types of heat exchanger used in the chemical process and allied industries, which will be discussed in this chapter, are listed below:

1. Double-pipe exchanger: the simplest type, used for cooling and heating.
2. Shell and tube exchangers: used for all applications.
3. Plate and frame exchangers (plate heat exchangers): used for heating and cooling.
4. Plate-fin exchangers.
5. Spiral heat exchangers.
6. Air cooled: coolers and condensers.
7. Direct contact: cooling and quenching.
8. Agitated vessels.
9. Fired heaters.

The word “exchanger” really applies to all types of equipment in which heat is exchanged but is often used specifically to denote equipment in which heat is exchanged between two process streams. Exchangers in which a process fluid is heated or cooled by a plant service stream are referred to as heaters and coolers. If the process stream is vaporised the exchanger is called a vaporiser if the stream is essentially completely vaporised; a reboiler if associated with a distillation column; and an evaporator if used to concentrate a solution (see Chapter 10). The term fired exchanger is used for exchangers heated by combustion gases, such as boilers; other exchangers are referred to as “unfired exchangers”.

## 12.2. BASIC DESIGN PROCEDURE AND THEORY

The general equation for heat transfer across a surface is:

$$Q = UA\Delta T_m \quad (12.1)$$

where  $Q$  = heat transferred per unit time,  $W$ ,

$U$  = the overall heat transfer coefficient,  $W/m^2\text{°C}$ ,

$A$  = heat-transfer area,  $m^2$ ,

$\Delta T_m$  = the mean temperature difference, the temperature driving force,  $\text{°C}$ .

The prime objective in the design of an exchanger is to determine the surface area required for the specified duty (rate of heat transfer) using the temperature differences available.

The overall coefficient is the reciprocal of the overall resistance to heat transfer, which is the sum of several individual resistances. For heat exchange across a typical heat-exchanger tube the relationship between the overall coefficient and the individual coefficients, which are the reciprocals of the individual resistances, is given by:

$$\frac{1}{U_o} = \frac{1}{h_o} + \frac{1}{h_{od}} + \frac{d_o \ln\left(\frac{d_o}{d_i}\right)}{2k_w} + \frac{d_o}{d_i} \times \frac{1}{h_{id}} + \frac{d_o}{d_i} \times \frac{1}{h_i} \quad (12.2)$$

where  $U_o$  = the overall coefficient based on the outside area of the tube,  $W/m^2\text{°C}$ ,

$h_o$  = outside fluid film coefficient,  $W/m^2\text{°C}$ ,

$h_i$  = inside fluid film coefficient,  $W/m^2\text{°C}$ ,

$h_{od}$  = outside dirt coefficient (fouling factor),  $W/m^2\text{°C}$ ,

$h_{id}$  = inside dirt coefficient,  $W/m^2\text{°C}$ ,

$k_w$  = thermal conductivity of the tube wall material,  $W/m\text{°C}$ ,

$d_i$  = tube inside diameter,  $m$ ,

$d_o$  = tube outside diameter,  $m$ .

The magnitude of the individual coefficients will depend on the nature of the heat-transfer process (conduction, convection, condensation, boiling or radiation), on the physical properties of the fluids, on the fluid flow-rates, and on the physical arrangement of the heat-transfer surface. As the physical layout of the exchanger cannot be determined until the area is known the design of an exchanger is of necessity a trial and error procedure. The steps in a typical design procedure are given below:

1. Define the duty: heat-transfer rate, fluid flow-rates, temperatures.
2. Collect together the fluid physical properties required: density, viscosity, thermal conductivity.
3. Decide on the type of exchanger to be used.
4. Select a trial value for the overall coefficient,  $U$ .
5. Calculate the mean temperature difference,  $\Delta T_m$ .
6. Calculate the area required from equation 12.1.
7. Decide the exchanger layout.
8. Calculate the individual coefficients.
9. Calculate the overall coefficient and compare with the trial value. If the calculated value differs significantly from the estimated value, substitute the calculated for the estimated value and return to step 6.
10. Calculate the exchanger pressure drop; if unsatisfactory return to steps 7 or 4 or 3, in that order of preference.
11. Optimise the design: repeat steps 4 to 10, as necessary, to determine the cheapest exchanger that will satisfy the duty. Usually this will be the one with the smallest area.

Procedures for estimating the individual heat-transfer coefficients and the exchanger pressure drops are given in this chapter.

### 12.2.1. Heat exchanger analysis: the effectiveness—NTU method

The *effectiveness—NTU* method is a procedure for evaluating the performance of heat exchangers, which has the advantage that it does not require the evaluation of the mean temperature differences. *NTU* stands for the Number of Transfer Units, and is analogous with the use of transfer units in mass transfer; see Chapter 11.

The principal use of this method is in the rating of an existing exchanger. It can be used to determine the performance of the exchanger when the heat transfer area and construction details are known. The method has an advantage over the use of the design procedure outlined above, as an unknown stream outlet temperature can be determined directly, without the need for iterative calculations. It makes use of plots of the exchanger *effectiveness* versus *NTU*. The effectiveness is the ratio of the actual rate of heat transfer, to the maximum possible rate.

The *effectiveness—NTU* method will not be covered in this book, as it is more useful for rating than design. The method is covered in books by Incropera and Dewitt (2001), Ozisik (1985) and Hewitt *et al.* (1994). The method is also covered by the Engineering Sciences Data Unit in their Design Guides 98003 to 98007 (1998). These guides give large clear plots of *effectiveness* versus *NTU* and are recommended for accurate work.

## 12.3. OVERALL HEAT-TRANSFER COEFFICIENT

Typical values of the overall heat-transfer coefficient for various types of heat exchanger are given in Table 12.1. More extensive data can be found in the books by Perry *et al.* (1997), TEMA (1999), and Ludwig (2001).

Table 12.1. Typical overall coefficients

<b>Shell and tube exchangers</b>		
Hot fluid	Cold fluid	$U$ (W/m <sup>2</sup> °C)
<i>Heat exchangers</i>		
Water	Water	800–1500
Organic solvents	Organic solvents	100–300
Light oils	Light oils	100–400
Heavy oils	Heavy oils	50–300
Gases	Gases	10–50
<i>Coolers</i>		
Organic solvents	Water	250–750
Light oils	Water	350–900
Heavy oils	Water	60–300
Gases	Water	20–300
Organic solvents	Brine	150–500
Water	Brine	600–1200
Gases	Brine	15–250
<i>Heaters</i>		
Steam	Water	1500–4000
Steam	Organic solvents	500–1000
Steam	Light oils	300–900
Steam	Heavy oils	60–450
Steam	Gases	30–300
Dowtherm	Heavy oils	50–300
Dowtherm	Gases	20–200
Flue gases	Steam	30–100
Flue	Hydrocarbon vapours	30–100
<i>Condensers</i>		
Aqueous vapours	Water	1000–1500
Organic vapours	Water	700–1000
Organics (some non-condensables)	Water	500–700
Vacuum condensers	Water	200–500
<i>Vaporisers</i>		
Steam	Aqueous solutions	1000–1500
Steam	Light organics	900–1200
Steam	Heavy organics	600–900
<b>Air-cooled exchangers</b>		
Process fluid		
Water		300–450
Light organics		300–700
Heavy organics		50–150
Gases, 5–10 bar		50–100
10–30 bar		100–300
Condensing hydrocarbons		300–600
<b>Immersed coils</b>		
Coil	Pool	
<i>Natural circulation</i>		
Steam	Dilute aqueous solutions	500–1000
Steam	Light oils	200–300
Steam	Heavy oils	70–150
Water	Aqueous solutions	200–500
Water	Light oils	100–150

(continued overleaf)

Table 12.1. (continued)

<b>Immersed coils</b>		
Coil	Pool	$U$ ( $W/m^2\text{ }^\circ\text{C}$ )
<i>Agitated</i>		
Steam	Dilute aqueous solutions	800–1500
Steam	Light oils	300–500
Steam	Heavy oils	200–400
Water	Aqueous solutions	400–700
Water	Light oils	200–300
<b>Jacketed vessels</b>		
Jacket	Vessel	
Steam	Dilute aqueous solutions	500–700
Steam	Light organics	250–500
Water	Dilute aqueous solutions	200–500
Water	Light organics	200–300
<b>Gasketed-plate exchangers</b>		
Hot fluid	Cold fluid	
Light organic	Light organic	2500–5000
Light organic	Viscous organic	250–500
Viscous organic	Viscous organic	100–200
Light organic	Process water	2500–3500
Viscous organic	Process water	250–500
Light organic	Cooling water	2000–4500
Viscous organic	Cooling water	250–450
Condensing steam	Light organic	2500–3500
Condensing steam	Viscous organic	250–500
Process water	Process water	5000–7500
Process water	Cooling water	5000–7000
Dilute aqueous solutions	Cooling water	5000–7000
Condensing steam	Process water	3500–4500

Figure 12.1, which is adapted from a similar nomograph given by Frank (1974), can be used to estimate the overall coefficient for tubular exchangers (shell and tube). The film coefficients given in Figure 12.1 include an allowance for fouling.

The values given in Table 12.1 and Figure 12.1 can be used for the preliminary sizing of equipment for process evaluation, and as trial values for starting a detailed thermal design.

## 12.4. FOULING FACTORS (DIRT FACTORS)

Most process and service fluids will foul the heat-transfer surfaces in an exchanger to a greater or lesser extent. The deposited material will normally have a relatively low thermal conductivity and will reduce the overall coefficient. It is therefore necessary to oversize an exchanger to allow for the reduction in performance during operation. The effect of fouling is allowed for in design by including the inside and outside fouling coefficients in equation 12.2. Fouling factors are usually quoted as heat-transfer resistances, rather than coefficients. They are difficult to predict and are usually based on past experience.

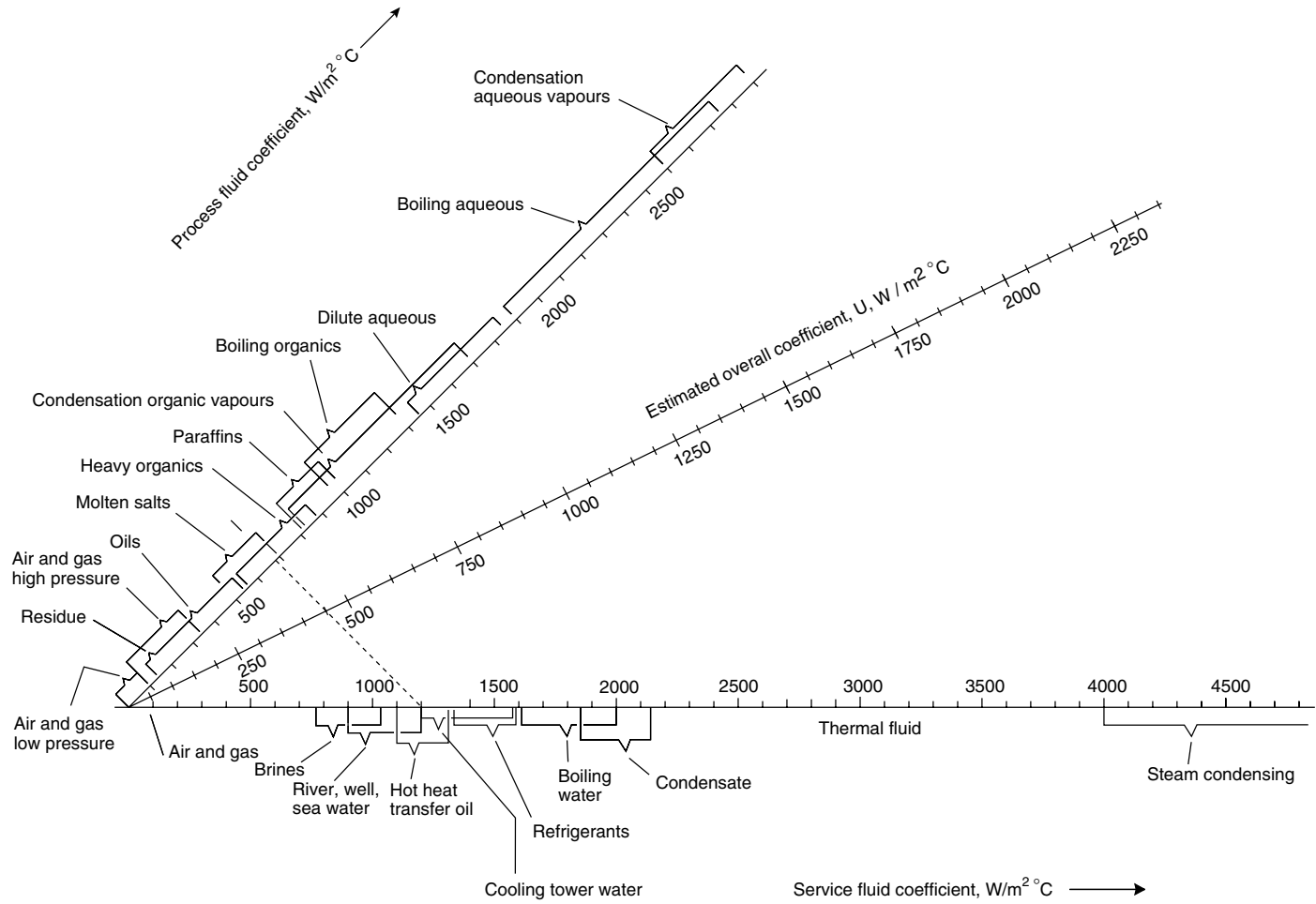


Figure 12.1. Overall coefficients (join process side duty to service side and read  $U$  from centre scale)



Estimating fouling factors introduces a considerable uncertainty into exchanger design; the value assumed for the fouling factor can overwhelm the accuracy of the predicted values of the other coefficients. Fouling factors are often wrongly used as factors of safety in exchanger design. Some work on the prediction of fouling factors has been done by HTRI; see Taborek *et al.* (1972). Fouling is the subject of books by Bott (1990) and Garrett-Price (1985).

Typical values for the fouling coefficients and factors for common process and service fluids are given in Table 12.2. These values are for shell and tube exchangers with plain (not finned) tubes. More extensive data on fouling factors are given in the TEMA standards (1999), and by Ludwig (2001).

Table 12.2. Fouling factors (coefficients), typical values

Fluid	Coefficient (W/m <sup>2</sup> °C)	Factor (resistance) (m <sup>2</sup> C/W)
River water	3000–12,000	0.0003–0.0001
Sea water	1000–3000	0.001–0.0003
Cooling water (towers)	3000–6000	0.0003–0.00017
Towns water (soft)	3000–5000	0.0003–0.0002
Towns water (hard)	1000–2000	0.001–0.0005
Steam condensate	1500–5000	0.00067–0.0002
Steam (oil free)	4000–10,000	0.0025–0.0001
Steam (oil traces)	2000–5000	0.0005–0.0002
Refrigerated brine	3000–5000	0.0003–0.0002
Air and industrial gases	5000–10,000	0.0002–0.0001
Flue gases	2000–5000	0.0005–0.0002
Organic vapours	5000	0.0002
Organic liquids	5000	0.0002
Light hydrocarbons	5000	0.0002
Heavy hydrocarbons	2000	0.0005
Boiling organics	2500	0.0004
Condensing organics	5000	0.0002
Heat transfer fluids	5000	0.0002
Aqueous salt solutions	3000–5000	0.0003–0.0002

The selection of the design fouling coefficient will often be an economic decision. The optimum design will be obtained by balancing the extra capital cost of a larger exchanger against the savings in operating cost obtained from the longer operating time between cleaning that the larger area will give. Duplicate exchangers should be considered for severely fouling systems.

## 12.5. SHELL AND TUBE EXCHANGERS: CONSTRUCTION DETAILS

The shell and tube exchanger is by far the most commonly used type of heat-transfer equipment used in the chemical and allied industries. The advantages of this type are:

1. The configuration gives a large surface area in a small volume.
2. Good mechanical layout: a good shape for pressure operation.
3. Uses well-established fabrication techniques.
4. Can be constructed from a wide range of materials.

5. Easily cleaned.
6. Well-established design procedures.

Essentially, a shell and tube exchanger consists of a bundle of tubes enclosed in a cylindrical shell. The ends of the tubes are fitted into tube sheets, which separate the shell-side and tube-side fluids. Baffles are provided in the shell to direct the fluid flow and support the tubes. The assembly of baffles and tubes is held together by support rods and spacers, Figure 12.2.

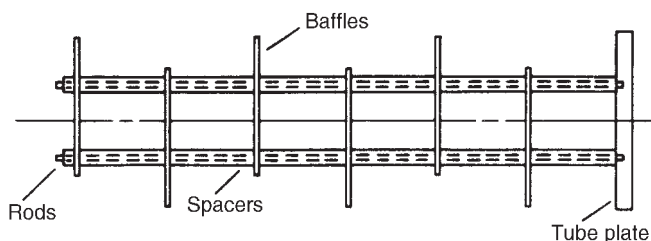


Figure 12.2. Baffle spacers and tie rods

### **Exchanger types**

The principal types of shell and tube exchanger are shown in Figures 12.3 to 12.8. Diagrams of other types and full details of their construction can be found in the heat-exchanger standards (see Section 12.5.1.). The standard nomenclature used for shell and tube exchangers is given below; the numbers refer to the features shown in Figures 12.3 to 12.8.

### **Nomenclature**

Part number

- |  |  |
|--|--|
| 1. Shell                               | 15. Floating-head support              |
| 2. Shell cover                         | 16. Weir                               |
| 3. Floating-head cover                 | 17. Split ring                         |
| 4. Floating-tube plate                 | 18. Tube                               |
| 5. Clamp ring                          | 19. Tube bundle                        |
| 6. Fixed-tube sheet (tube plate)       | 20. Pass partition                     |
| 7. Channel (end-box or header)         | 21. Floating-head gland (packed gland) |
| 8. Channel cover                       | 22. Floating-head gland ring           |
| 9. Branch (nozzle)                     | 23. Vent connection                    |
| 10. Tie rod and spacer                 | 24. Drain connection                   |
| 11. Cross baffle or tube-support plate | 25. Test connection                    |
| 12. Impingement baffle                 | 26. Expansion bellows                  |
| 13. Longitudinal baffle                | 27. Lifting ring                       |
| 14. Support bracket                    |  |

The simplest and cheapest type of shell and tube exchanger is the fixed tube sheet design shown in Figure 12.3. The main disadvantages of this type are that the tube bundle cannot be removed for cleaning and there is no provision for differential expansion of the shell and tubes. As the shell and tubes will be at different temperatures, and may be of different materials, the differential expansion can be considerable and the use of this type is limited to temperature differences up to about 80°C. Some provision for expansion can be made by including an expansion loop in the shell (shown dotted on Figure 12.3) but their use is limited to low shell pressure; up to about 8 bar. In the other types, only one end of the tubes is fixed and the bundle can expand freely.

The U-tube (U-bundle) type shown in Figure 12.4 requires only one tube sheet and is cheaper than the floating-head types; but is limited in use to relatively clean fluids as the tubes and bundle are difficult to clean. It is also more difficult to replace a tube in this type.

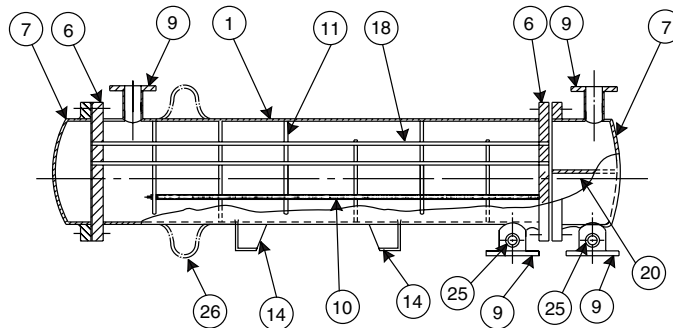


Figure 12.3. Fixed-tube plate (based on figures from BS 3274: 1960)

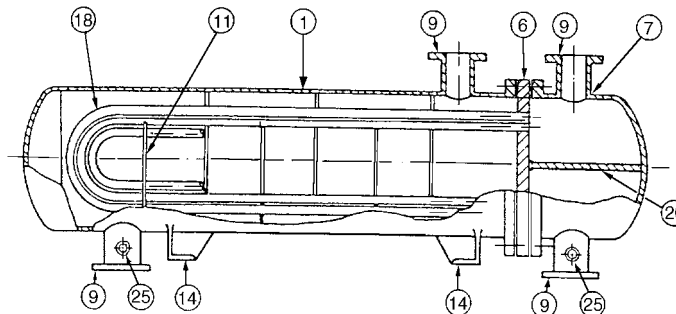


Figure 12.4. U-tube (based on figures from BS 3274: 1960)

Exchangers with an internal floating head, Figures 12.5 and 12.6, are more versatile than fixed head and U-tube exchangers. They are suitable for high-temperature differentials

and, as the tubes can be rodded from end to end and the bundle removed, are easier to clean and can be used for fouling liquids. A disadvantage of the pull-through design, Figure 12.5, is that the clearance between the outermost tubes in the bundle and the shell must be made greater than in the fixed and U-tube designs to accommodate the floating-head flange, allowing fluid to bypass the tubes. The clamp ring (split flange design), Figure 12.6, is used to reduce the clearance needed. There will always be a danger of leakage occurring from the internal flanges in these floating head designs.

In the external floating head designs, Figure 12.7, the floating-head joint is located outside the shell, and the shell sealed with a sliding gland joint employing a stuffing box. Because of the danger of leaks through the gland, the shell-side pressure in this type is usually limited to about 20 bar, and flammable or toxic materials should not be used on the shell side.

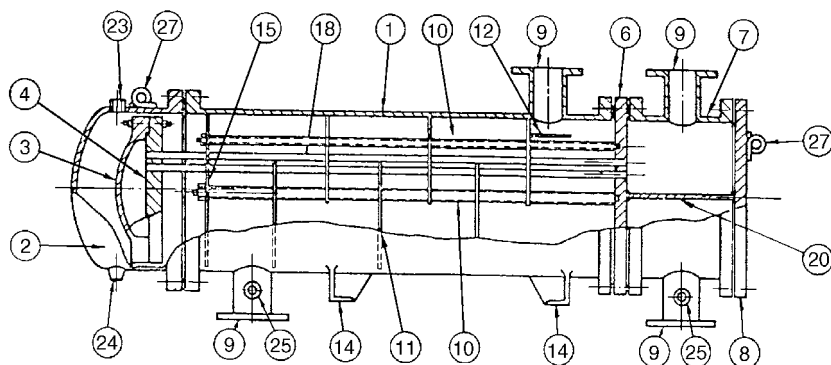


Figure 12.5. Internal floating head without clamp ring (based on figures from BS 3274: 1960)

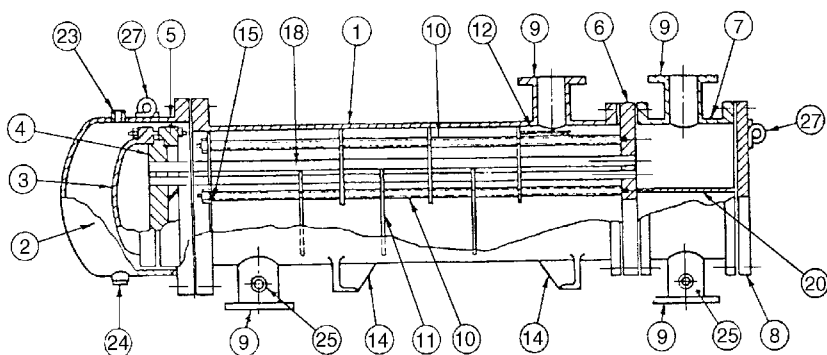


Figure 12.6. Internal floating head with clamp ring (based on figures from BS 3274: 1960)

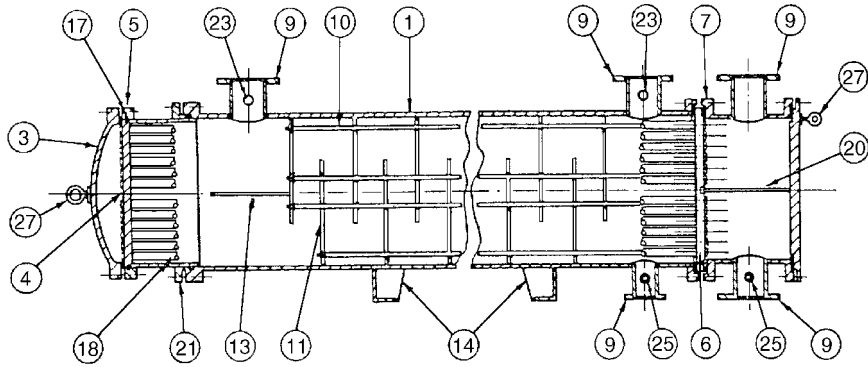


Figure 12.7. External floating head, packed gland (based on figures from BS 3274: 1960)

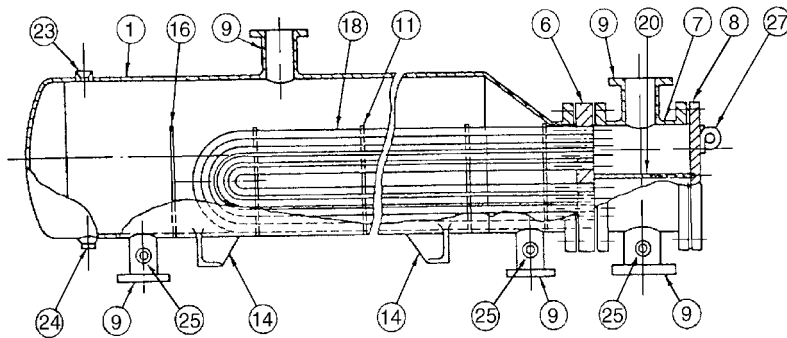


Figure 12.8. Kettle reboiler with U-tube bundle (based on figures from BS 3274: 1960)

### 12.5.1. Heat-exchanger standards and codes

The mechanical design features, fabrication, materials of construction, and testing of shell and tube exchangers is covered by British Standard, BS 3274. The standards of the American Tubular Heat Exchanger Manufacturers Association, the TEMA standards, are also universally used. The TEMA standards cover three classes of exchanger: class R covers exchangers for the generally severe duties of the petroleum and related industries; class C covers exchangers for moderate duties in commercial and general process applications; and class B covers exchangers for use in the chemical process industries. The British and American standards should be consulted for full details of the mechanical design features of shell and tube exchangers; only brief details will be given in this chapter.

The standards give the preferred shell and tube dimensions; the design and manufacturing tolerances; corrosion allowances; and the recommended design stresses for materials of construction. The shell of an exchanger is a pressure vessel and will be designed in accordance with the appropriate national pressure vessel code or standard; see Chapter 13, Section 13.2. The dimensions of standard flanges for use with heat exchangers are given in BS 3274, and in the TEMA standards.

In both the American and British standards dimensions are given in feet and inches, so these units have been used in this chapter with the equivalent values in SI units given in brackets.

## 12.5.2. Tubes

### *Dimensions*

Tube diameters in the range  $\frac{5}{8}$  in. (16 mm) to 2 in. (50 mm) are used. The smaller diameters  $\frac{5}{8}$  to 1 in. (16 to 25 mm) are preferred for most duties, as they will give more compact, and therefore cheaper, exchangers. Larger tubes are easier to clean by mechanical methods and would be selected for heavily fouling fluids.

The tube thickness (gauge) is selected to withstand the internal pressure and give an adequate corrosion allowance. Steel tubes for heat exchangers are covered by BS 3606 (metric sizes); the standards applicable to other materials are given in BS 3274. Standard diameters and wall thicknesses for steel tubes are given in Table 12.3.

Table 12.3. Standard dimensions for steel tubes

Outside diameter (mm)		Wall thickness (mm)				
16	1.2	1.6	2.0	—	—	—
20	—	1.6	2.0	2.6	—	—
25	—	1.6	2.0	2.6	3.2	—
30	—	1.6	2.0	2.6	3.2	—
38	—	—	2.0	2.6	3.2	—
50	—	—	2.0	2.6	3.2	—

The preferred lengths of tubes for heat exchangers are: 6 ft. (1.83 m), 8 ft (2.44 m), 12 ft (3.66 m), 16 ft (4.88 m) 20 ft (6.10 m), 24 ft (7.32 m). For a given surface area, the use of longer tubes will reduce the shell diameter; which will generally result in a lower cost exchanger, particularly for high shell pressures. The optimum tube length to shell diameter will usually fall within the range of 5 to 10.

If U-tubes are used, the tubes on the outside of the bundle will be longer than those on the inside. The average length needs to be estimated for use in the thermal design. U-tubes will be bent from standard tube lengths and cut to size.

The tube size is often determined by the plant maintenance department standards, as clearly it is an advantage to reduce the number of sizes that have to be held in stores for tube replacement.

As a guide,  $\frac{3}{4}$  in. (19 mm) is a good trial diameter with which to start design calculations.

### *Tube arrangements*

The tubes in an exchanger are usually arranged in an equilateral triangular, square, or rotated square pattern; see Figure 12.9.

The triangular and rotated square patterns give higher heat-transfer rates, but at the expense of a higher pressure drop than the square pattern. A square, or rotated square arrangement, is used for heavily fouling fluids, where it is necessary to mechanically clean

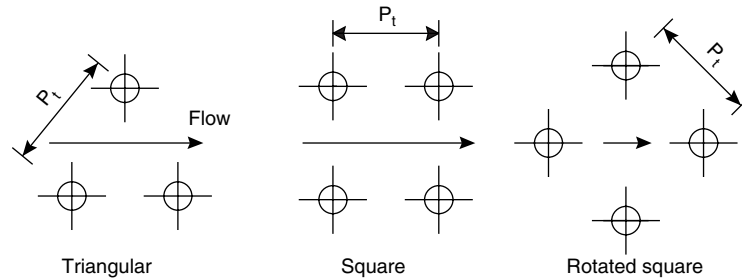


Figure 12.9. Tube patterns

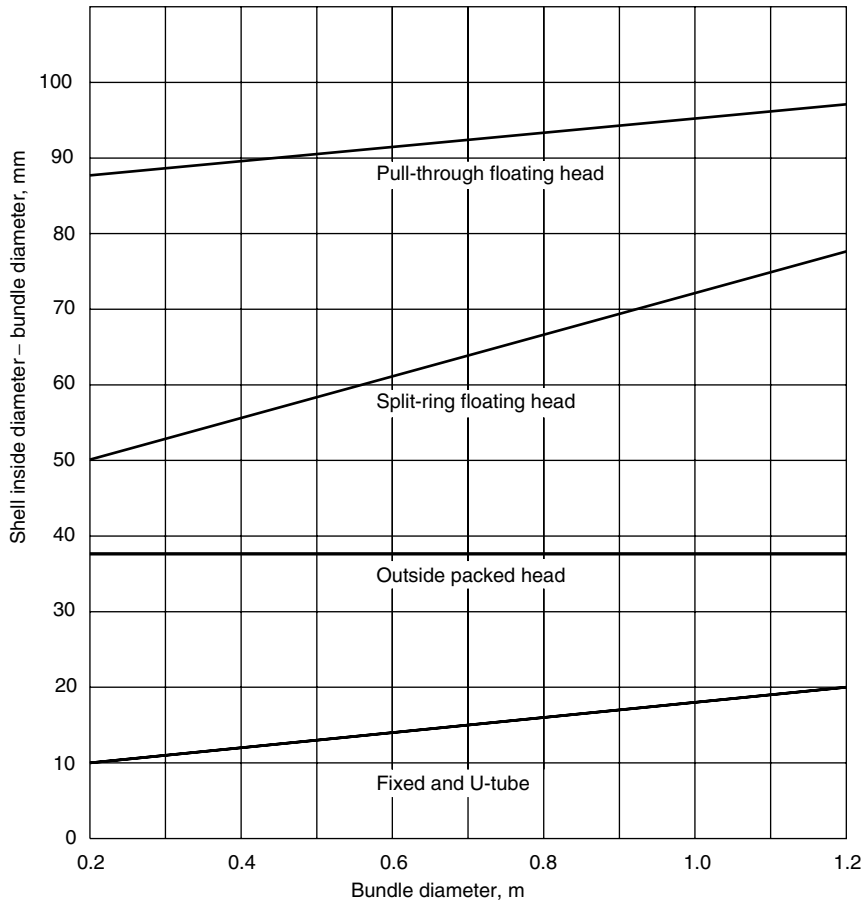


Figure 12.10. Shell-bundle clearance

the outside of the tubes. The recommended tube pitch (distance between tube centres) is 1.25 times the tube outside diameter; and this will normally be used unless process requirements dictate otherwise. Where a square pattern is used for ease of cleaning, the recommended minimum clearance between the tubes is 0.25 in. (6.4 mm).

### ***Tube-side passes***

The fluid in the tube is usually directed to flow back and forth in a number of “passes” through groups of tubes arranged in parallel, to increase the length of the flow path. The number of passes is selected to give the required tube-side design velocity. Exchangers are built with from one to up to about sixteen tube passes. The tubes are arranged into the number of passes required by dividing up the exchanger headers (channels) with partition plates (pass partitions). The arrangement of the pass partitions for 2, 4 and 6 tube passes are shown in Figure 12.11. The layouts for higher numbers of passes are given by Saunders (1988).

### **12.5.3. Shells**

The British standard BS 3274 covers exchangers from 6 in. (150 mm) to 42 in. (1067 mm) diameter; and the TEMA standards, exchangers up to 60 in. (1520 mm).

Up to about 24 in. (610 mm) shells are normally constructed from standard, close tolerance, pipe; above 24 in. (610 mm) they are rolled from plate.

For pressure applications the shell thickness would be sized according to the pressure vessel design standards, see Chapter 13. The minimum allowable shell thickness is given in BS 3274 and the TEMA standards. The values, converted to SI units and rounded, are given below:

#### ***Minimum shell thickness***

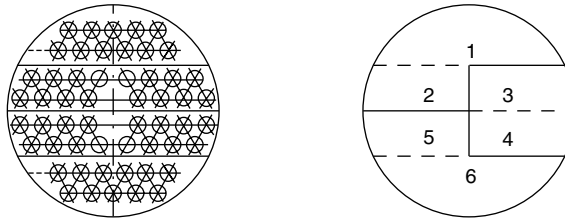
Nominal shell dia., mm	Carbon steel		Alloy steel
	pipe	plate	
150	7.1	—	3.2
200–300	9.3	—	3.2
330–580	9.5	7.9	3.2
610–740	—	7.9	4.8
760–990	—	9.5	6.4
1010–1520	—	11.1	6.4
1550–2030	—	12.7	7.9
2050–2540	—	12.7	9.5

The shell diameter must be selected to give as close a fit to the tube bundle as is practical; to reduce bypassing round the outside of the bundle; see Section 12.9. The clearance required between the outermost tubes in the bundle and the shell inside diameter will depend on the type of exchanger and the manufacturing tolerances; typical values are given in Figure 12.10 (as given on p. 646).

### **12.5.4. Tube-sheet layout (tube count)**

The bundle diameter will depend not only on the number of tubes but also on the number of tube passes, as spaces must be left in the pattern of tubes on the tube sheet to accommodate the pass partition plates.





Six tube passes



Four passes



Two passes

Figure 12.11. Tube arrangements, showing pass-partitions in headers

An estimate of the bundle diameter  $D_b$  can be obtained from equation 12.3b, which is an empirical equation based on standard tube layouts. The constants for use in this equation, for triangular and square patterns, are given in Table 12.4.

$$N_t = K_1 \left( \frac{D_b}{d_o} \right)^{n_1}, \quad (12.3a)$$

$$D_b = d_o \left( \frac{N_t}{K_1} \right)^{1/n_1}, \quad (12.3b)$$

where  $N_t$  = number of tubes,

$D_b$  = bundle diameter, mm,

$d_o$  = tube outside diameter, mm.

If U-tubes are used the number of tubes will be slightly less than that given by equation 12.3a, as the spacing between the two centre rows will be determined by the minimum allowable radius for the U-bend. The minimum bend radius will depend on the tube diameter and wall thickness. It will range from 1.5 to 3.0 times the tube outside diameter. The tighter bend radius will lead to some thinning of the tube wall.

An estimate of the number of tubes in a U-tube exchanger (twice the actual number of U-tubes), can be made by reducing the number given by equation 12.3a by one centre row of tubes.

The number of tubes in the centre row, the row at the shell equator, is given by:

$$\text{Tubes in centre row} = \frac{D_b}{P_t}$$

where  $p_t$  = tube pitch, mm.

The tube layout for a particular design will normally be planned with the aid of computer programs. These will allow for the spacing of the pass partition plates and the position of the tie rods. Also, one or two rows of tubes may be omitted at the top and bottom of the bundle to increase the clearance and flow area opposite the inlet and outlet nozzles.

Tube count tables which give an estimate of the number of tubes that can be accommodated in standard shell sizes, for commonly used tube sizes, pitches and number of passes, can be found in several books: Kern (1950), Ludwig (2001), Perry *et al.* (1997), and Saunders (1988).

Some typical tube arrangements are shown in Appendix I.

Table 12.4. Constants for use in equation 12.3

Triangular pitch, $p_t = 1.25d_o$					
No. passes	1	2	4	6	8
$K_1$	0.319	0.249	0.175	0.0743	0.0365
$n_1$	2.142	2.207	2.285	2.499	2.675
Square pitch, $p_t = 1.25d_o$					
No. passes	1	2	4	6	8
$K_1$	0.215	0.156	0.158	0.0402	0.0331
$n_1$	2.207	2.291	2.263	2.617	2.643

### 12.5.5. Shell types (passes)

The principal shell arrangements are shown in Figure 12.12a–e. The letters E, F, G, H, J are those used in the TEMA standards to designate the various types. The E shell is the most commonly used arrangement.

Two shell passes (F shell) are occasionally used where the shell and tube side temperature differences will be unsuitable for a single pass (see Section 12.6). However, it is difficult to obtain a satisfactory seal with a shell-side baffle and the same flow arrangement can be achieved by using two shells in series. One method of sealing the longitudinal shell-side baffle is shown in Figure 12.12f.

The divided flow and split-flow arrangements (G and J shells) are used to reduce the shell-side pressure drop; where pressure drop, rather than heat transfer, is the controlling factor in the design.

### 12.5.6. Shell and tube designation

A common method of describing an exchanger is to designate the number of shell and tube passes:  $m/n$ ; where  $m$  is the number of shell passes and  $n$  the number of tube passes.

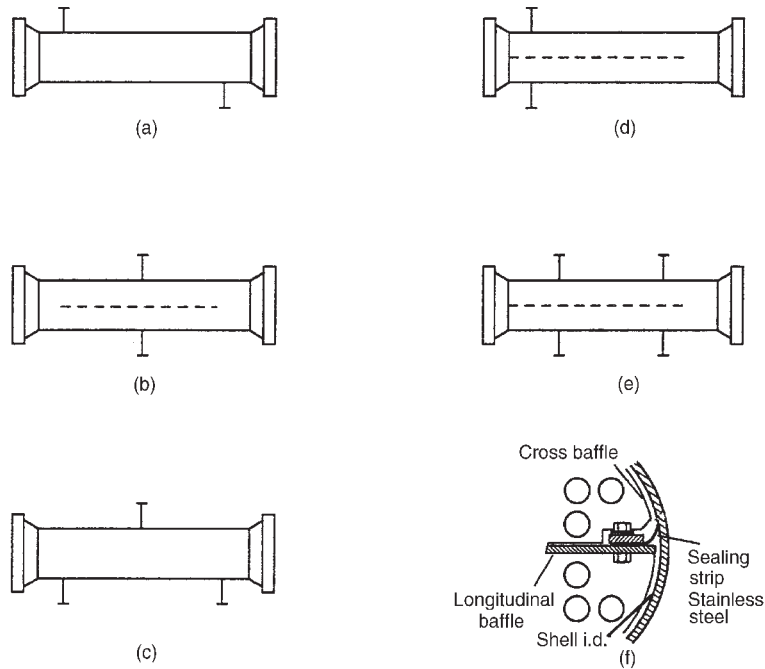


Figure 12.12. Shell types (pass arrangements). (a) One-pass shell (E shell) (b) Split flow (G shell) (c) Divided flow (J shell) (d) Two-pass shell with longitudinal baffle (F shell) (e) Double split flow (H shell)

So 1/2 describes an exchanger with 1 shell pass and 2 tube passes, and 2/4 an exchanger with 2 shell passes and 4 tube passes.

### 12.5.7. Baffles

Baffles are used in the shell to direct the fluid stream across the tubes, to increase the fluid velocity and so improve the rate of transfer. The most commonly used type of baffle is the single segmental baffle shown in Figure 12.13a, other types are shown in Figures 12.13b, c and d.

Only the design of exchangers using single segmental baffles will be considered in this chapter.

If the arrangement shown in Figure 12.13a were used with a horizontal condenser the baffles would restrict the condensate flow. This problem can be overcome either by rotating the baffle arrangement through  $90^\circ$ , or by trimming the base of the baffle, Figure 12.14.

The term “baffle cut” is used to specify the dimensions of a segmental baffle. The baffle cut is the height of the segment removed to form the baffle, expressed as a percentage of the baffle disc diameter. Baffle cuts from 15 to 45 per cent are used. Generally, a baffle cut of 20 to 25 per cent will be the optimum, giving good heat-transfer rates, without excessive drop. There will be some leakage of fluid round the baffle as a clearance must be allowed for assembly. The clearance needed will depend on the shell diameter; typical values, and tolerances, are given in Table 12.5.

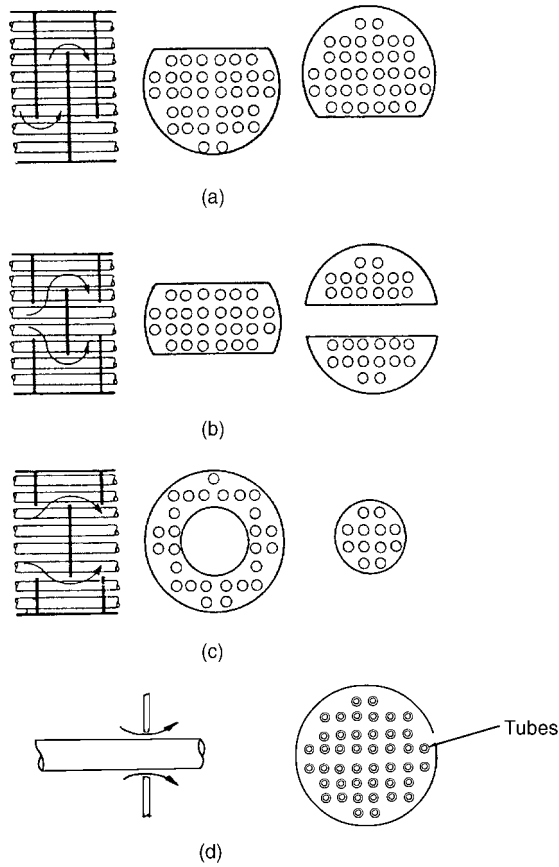


Figure 12.13. Types of baffle used in shell and tube heat exchangers. (a) Segmental (b) Segmental and strip (c) Disc and doughnut (d) Orifice

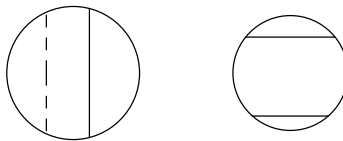


Figure 12.14. Baffles for condensers

Table 12.5. Typical baffle clearances and tolerances

Shell diameter, $D_s$	Baffle diameter	Tolerance
Pipe shells		
6 to 25 in. (152 to 635 mm)	$D_s - \frac{1}{16}$ in. (1.6 mm)	$+\frac{1}{32}$ in. (0.8 mm)
Plate shells		
6 to 25 in. (152 to 635 mm)	$D_s - \frac{1}{8}$ in. (3.2 mm)	$+0, -\frac{1}{32}$ in. (0.8 mm)
27 to 42 in. (686 to 1067 mm)	$D_s - \frac{3}{16}$ in. (4.8 mm)	$+0, -\frac{1}{16}$ in. (1.6 mm)

Another leakage path occurs through the clearance between the tube holes in the baffle and the tubes. The maximum design clearance will normally be  $\frac{1}{32}$  in. (0.8 mm).

The minimum thickness to be used for baffles and support plates are given in the standards. The baffle spacings used range from 0.2 to 1.0 shell diameters. A close baffle spacing will give higher heat transfer coefficients but at the expense of higher pressure drop. The optimum spacing will usually be between 0.3 to 0.5 times the shell diameter.

### 12.5.8. Support plates and tie rods

Where segmental baffles are used some will be fabricated with closer tolerances,  $\frac{1}{64}$  in. (0.4 mm), to act as support plates. For condensers and vaporisers, where baffles are not needed for heat-transfer purposes, a few will be installed to support the tubes.

The minimum spacings to be used for support plates are given in the standards. The spacing ranges from around 1 m for 16 mm tubes to 2 m for 25 mm tubes.

The baffles and support plate are held together with tie rods and spacers. The number of rods required will depend on the shell diameter, and will range from 4, 16 mm diameter rods, for exchangers under 380 mm diameter; to 8, 12.5 mm rods, for exchangers of 1 m diameter. The recommended number for a particular diameter can be found in the standards.

### 12.5.9. Tube sheets (plates)

In operation the tube sheets are subjected to the differential pressure between shell and tube sides. The design of tube sheets as pressure-vessel components is covered by BS 5500 and is discussed in Chapter 13. Design formulae for calculating tube sheet thicknesses are also given in the TEMA standards.

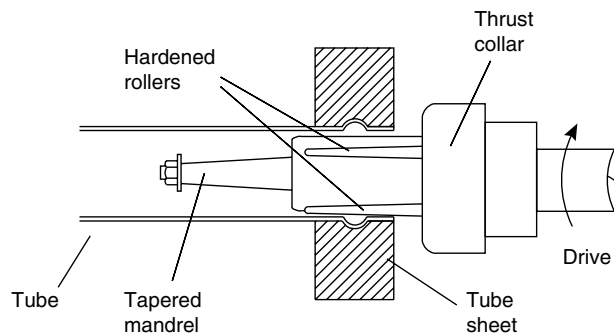


Figure 12.15. Tube rolling

The joint between the tubes and tube sheet is normally made by expanding the tube by rolling with special tools, Figure 12.15. Tube rolling is a skilled task; the tube must be expanded sufficiently to ensure a sound leak-proof joint, but not overthinned, weakening the tube. The tube holes are normally grooved, Figure 12.16a, to lock the tubes more firmly in position and to prevent the joint from being loosened by the differential expansion

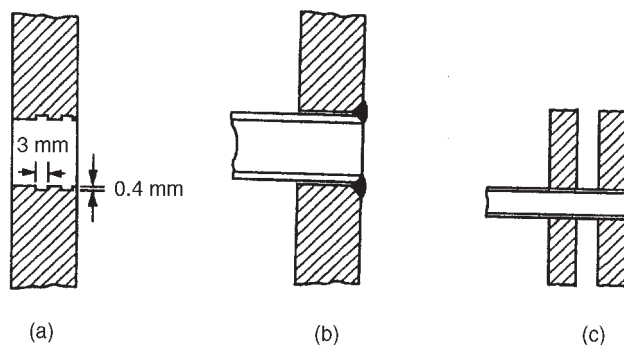


Figure 12.16. Tube/tube sheet joints

of the shell and tubes. When it is essential to guarantee a leak-proof joint the tubes can be welded to the sheet, Figure 12.16*b*. This will add to the cost of the exchanger; not only due to the cost of welding, but also because a wider tube spacing will be needed.

The tube sheet forms the barrier between the shell and tube fluids, and where it is essential for safety or process reasons to prevent any possibility of intermixing due to leakage at the tube sheet joint, double tube-sheets can be used, with the space between the sheets vented; Figure 12.16*c*.

To allow sufficient thickness to seal the tubes the tube sheet thickness should not be less than the tube outside diameter, up to about 25 mm diameter. Recommended minimum plate thicknesses are given in the standards.

The thickness of the tube sheet will reduce the effective length of the tube slightly, and this should be allowed for when calculating the area available for heat transfer. As a first approximation the length of the tubes can be reduced by 25 mm for each tube sheet.

### 12.5.10. Shell and header nozzles (branches)

Standard pipe sizes will be used for the inlet and outlet nozzles. It is important to avoid flow restrictions at the inlet and outlet nozzles to prevent excessive pressure drop and flow-induced vibration of the tubes. As well as omitting some tube rows (see Section 12.5.4), the baffle spacing is usually increased in the nozzle zone, to increase the flow area. For vapours and gases, where the inlet velocities will be high, the nozzle may be flared, or special designs used, to reduce the inlet velocities; Figure 12.17*a* and *b* (see p. 654). The extended shell design shown in Figure 12.17*b* also serves as an impingement plate. Impingement plates are used where the shell-side fluid contains liquid drops, or for high-velocity fluids containing abrasive particles.

### 12.5.11. Flow-induced tube vibrations

Premature failure of exchanger tubes can occur through vibrations induced by the shell-side fluid flow. Care must be taken in the mechanical design of large exchangers where

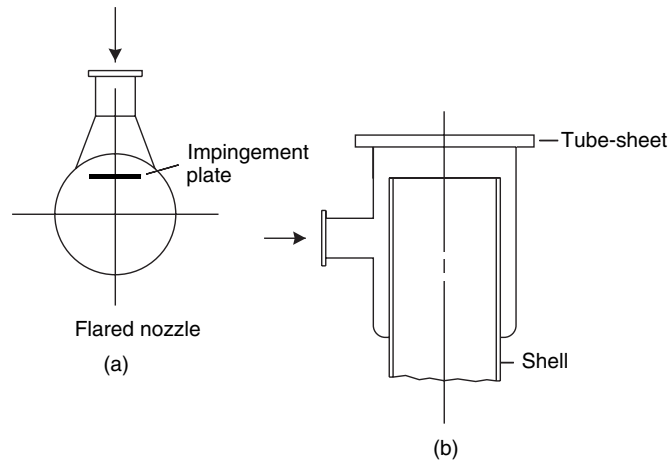


Figure 12.17. Inlet nozzle designs

the shell-side velocity is high, say greater than 3 m/s, to ensure that tubes are adequately supported.

The vibration induced by the fluid flowing over the tube bundle is caused principally by vortex shedding and turbulent buffeting. As fluid flows over a tube vortices are shed from the down-stream side which cause disturbances in the flow pattern and pressure distribution round the tube. Turbulent buffeting of tubes occurs at high flow-rates due to the intense turbulence at high Reynolds numbers.

The buffeting caused by vortex shedding or by turbulent eddies in the flow stream will cause vibration, but large amplitude vibrations will normally only occur above a certain critical flow velocity. Above this velocity the interaction with the adjacent tubes can provide a feed back path which reinforces the vibrations. Resonance will also occur if the vibrations approach the natural vibration frequency of the unsupported tube length. Under these conditions the magnitude of the vibrations can increase dramatically leading to tube failure. Failure can occur either through the impact of one tube on another or through wear on the tube where it passes through the baffles.

For most exchanger designs, following the recommendations on support sheet spacing given in the standards will be sufficient to protect against premature tube failure from vibration. For large exchangers with high velocities on the shell-side the design should be analysed to check for possible vibration problems. The computer aided design programs for shell-and-tube exchanger design available from commercial organisations, such as HTFS and HTRI (see Section 12.1), include programs for vibration analysis.

Much work has been done on tube vibration over the past 20 years, due to an increase in the failure of exchangers as larger sizes and higher flow-rates have been used. Discussion of this work is beyond the scope of this book; for review of the methods used see Saunders (1988) and Singh and Soler (1992).

See also, the Engineering Science Data Unit Design Guide ESDU 87019, which gives a clear explanation of mechanisms causing tube vibration in shell and tube heat exchangers, and their prediction and prevention.

## 12.6. MEAN TEMPERATURE DIFFERENCE (TEMPERATURE DRIVING FORCE)

Before equation 12.1 can be used to determine the heat transfer area required for a given duty, an estimate of the mean temperature difference  $\Delta T_m$  must be made. This will normally be calculated from the terminal temperature differences: the difference in the fluid temperatures at the inlet and outlet of the exchanger. The well-known “logarithmic mean” temperature difference (see Volume 1, Chapter 9) is only applicable to sensible heat transfer in true co-current or counter-current flow (linear temperature-enthalpy curves). For counter-current flow, Figure 12.18*a*, the logarithmic mean temperature is given by:

$$\Delta T_{\text{lm}} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \frac{(T_1 - t_2)}{(T_2 - t_1)}} \quad (12.4)$$

where  $\Delta T_{\text{lm}}$  = log mean temperature difference,

$T_1$  = hot fluid temperature, inlet,

$T_2$  = hot fluid temperature, outlet,

$t_1$  = cold fluid temperature, inlet,

$t_2$  = cold fluid temperature, outlet.

The equation is the same for co-current flow, but the terminal temperature differences will be  $(T_1 - t_1)$  and  $(T_2 - t_2)$ . Strictly, equation 12.4 will only apply when there is no change in the specific heats, the overall heat-transfer coefficient is constant, and there are no heat losses. In design, these conditions can be assumed to be satisfied providing the temperature change in each fluid stream is not large.

In most shell and tube exchangers the flow will be a mixture of co-current, counter-current and cross flow. Figures 12.18*b* and *c* show typical temperature profiles for an exchanger with one shell pass and two tube passes (a 1 : 2 exchanger). Figure 12.18*c* shows a temperature cross, where the outlet temperature of the cold stream is above that of the hot stream.

The usual practice in the design of shell and tube exchangers is to estimate the “true temperature difference” from the logarithmic mean temperature by applying a correction factor to allow for the departure from true counter-current flow:

$$\Delta T_m = F_t \Delta T_{\text{lm}} \quad (12.5)$$

where  $\Delta T_m$  = true temperature difference, the mean temperature difference for use in the design equation 12.1,

$F_t$  = the temperature correction factor.

The correction factor is a function of the shell and tube fluid temperatures, and the number of tube and shell passes. It is normally correlated as a function of two dimensionless temperature ratios:

$$R = \frac{(T_1 - T_2)}{(t_2 - t_1)} \quad (12.6)$$



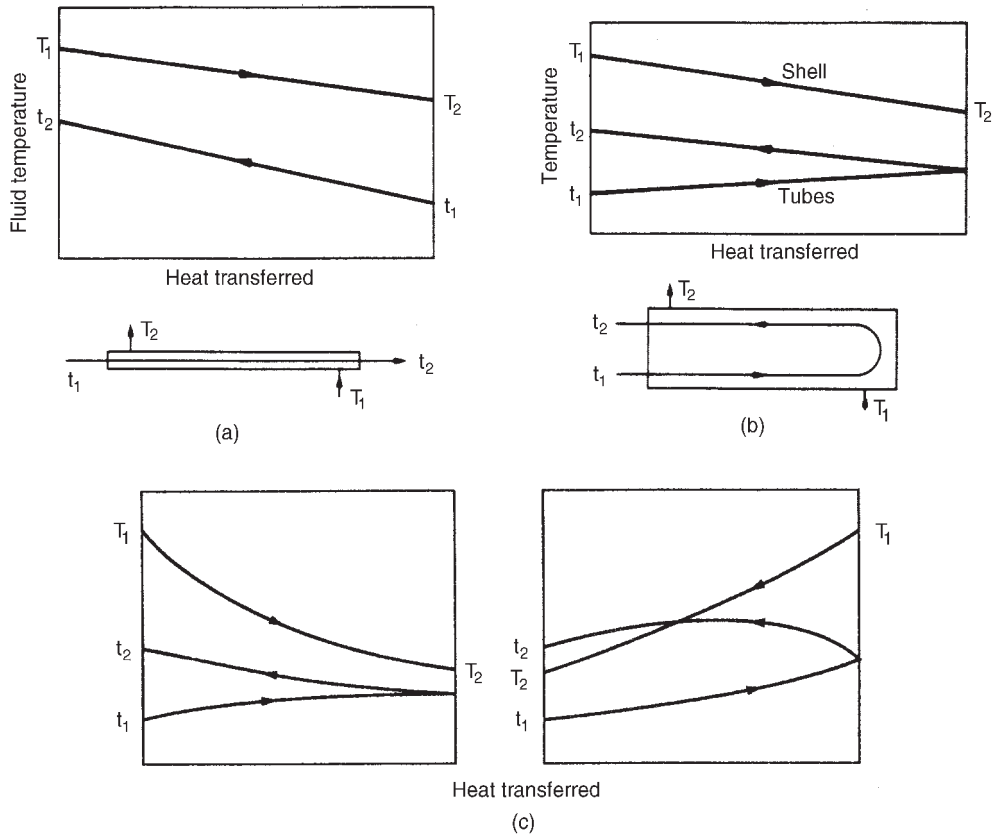


Figure 12.18. Temperature profiles (a) Counter-current flow (b) 1 : 2 exchanger (c) Temperature cross

and

$$S = \frac{(t_2 - t_1)}{(T_1 - t_1)} \quad (12.7)$$

$R$  is equal to the shell-side fluid flow-rate times the fluid mean specific heat; divided by the tube-side fluid flow-rate times the tube-side fluid specific heat.

$S$  is a measure of the temperature efficiency of the exchanger.

For a 1 shell : 2 tube pass exchanger, the correction factor is given by:

$$F_t = \frac{\sqrt{(R^2 + 1)} \ln \left[ \frac{(1 - S)}{(1 - RS)} \right]}{(R - 1) \ln \left[ \frac{2 - S[R + 1 - \sqrt{(R^2 + 1)}]}{2 - S[R + 1 + \sqrt{(R^2 + 1)}]} \right]} \quad (12.8)$$

The derivation of equation 12.8 is given by Kern (1950). The equation for a 1 shell : 2 tube pass exchanger can be used for any exchanger with an even number

of tube passes, and is plotted in Figure 12.19. The correction factor for 2 shell passes and 4, or multiples of 4, tube passes is shown in Figure 12.20, and that for divided and split flow shells in Figures 12.21 and 12.22.

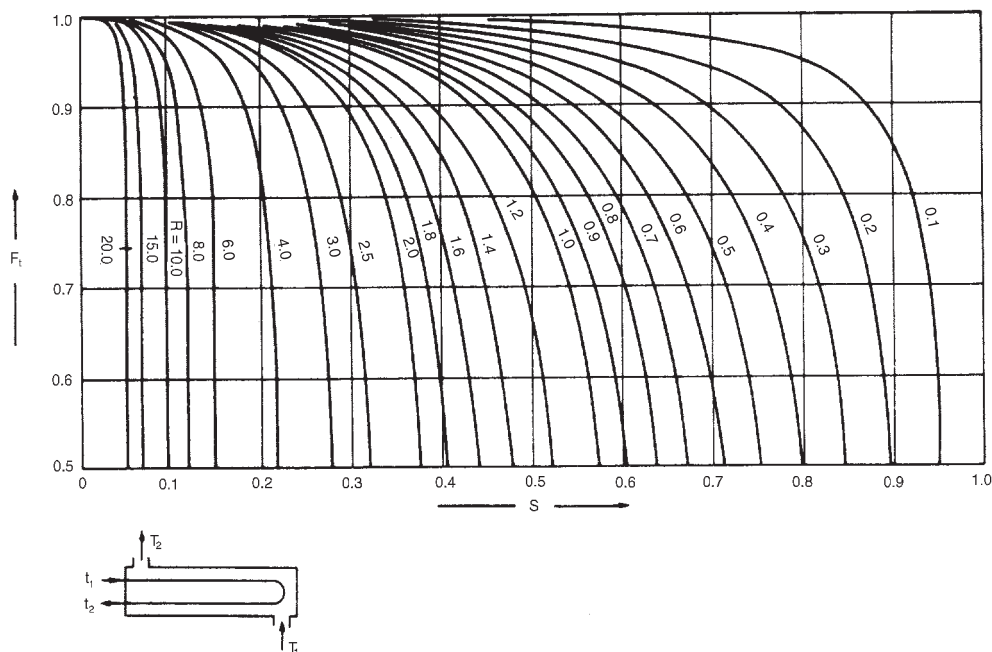


Figure 12.19. Temperature correction factor: one shell pass; two or more even tube passes

Temperature correction factor plots for other arrangements can be found in the TEMA standards and the books by Kern (1950) and Ludwig (2001). Mueller (1973) gives a comprehensive set of figures for calculating the log mean temperature correction factor, which includes figures for cross-flow exchangers.

The following assumptions are made in the derivation of the temperature correction factor  $F_t$ , in addition to those made for the calculation of the log mean temperature difference:

1. Equal heat transfer areas in each pass.
2. A constant overall heat-transfer coefficient in each pass.
3. The temperature of the shell-side fluid in any pass is constant across any cross-section.
4. There is no leakage of fluid between shell passes.

Though these conditions will not be strictly satisfied in practical heat exchangers, the  $F_t$  values obtained from the curves will give an estimate of the “true mean temperature difference” that is sufficiently accurate for most designs. Mueller (1973) discusses these

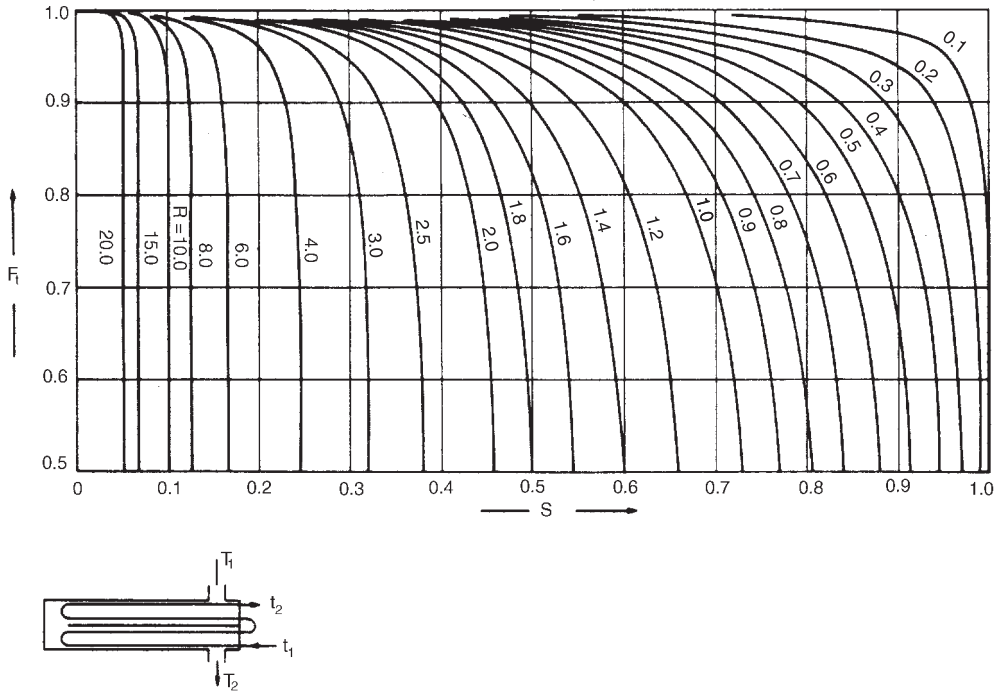


Figure 12.20. Temperature correction factor: two shell passes; four or multiples of four tube passes

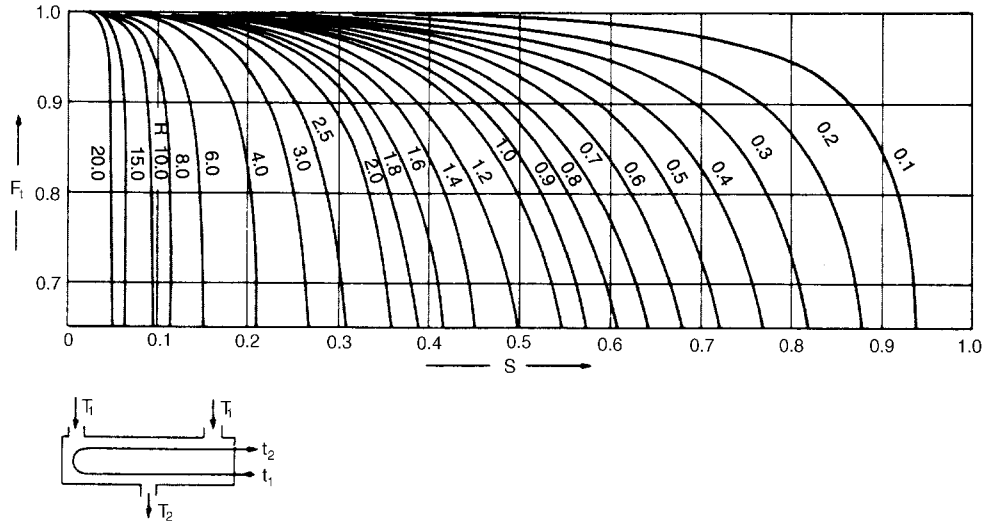


Figure 12.21. Temperature correction factor: divided-flow shell; two or more even-tube passes

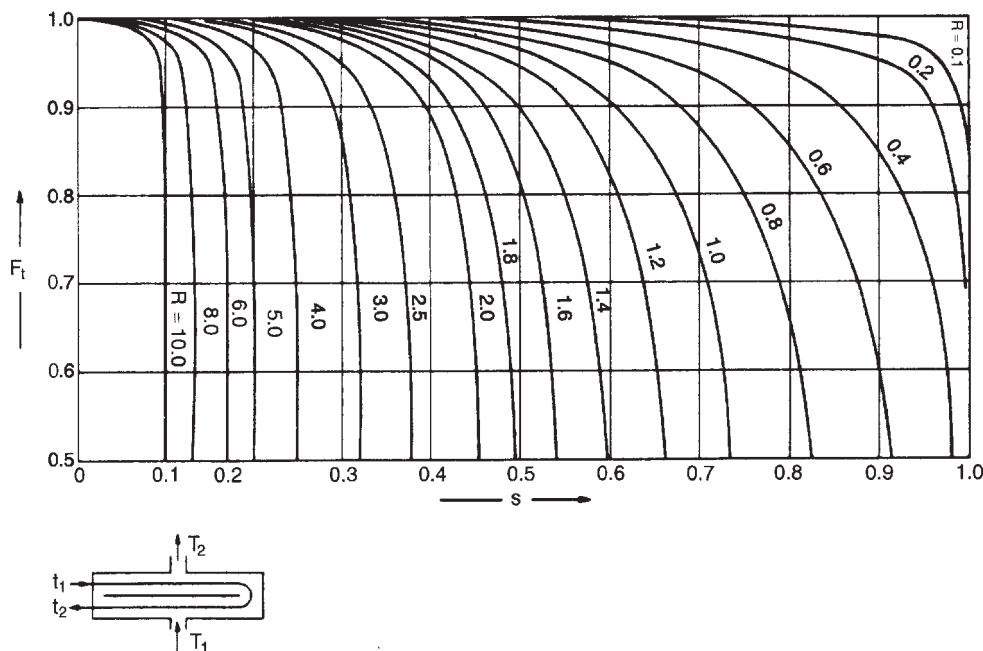


Figure 12.22. Temperature correction factor, split flow shell, 2 tube pass

assumptions, and gives  $F_t$  curves for conditions when all the assumptions are not met; see also Butterworth (1973) and Emerson (1973).

The shell-side leakage and bypass streams (see Section 12.9) will affect the mean temperature difference, but are not normally taken into account when estimating the correction factor  $F_t$ . Fisher and Parker (1969) give curves which show the effect of leakage on the correction factor for a 1 shell pass : 2 tube pass exchanger.

The value of  $F_t$  will be close to one when the terminal temperature differences are large, but will appreciably reduce the logarithmic mean temperature difference when the temperatures of shell and tube fluids approach each other; it will fall drastically when there is a temperature cross. A temperature cross will occur if the outlet temperature of the cold stream is greater than the inlet temperature of the hot stream, Figure 12.18c.

Where the  $F_t$  curve is near vertical values cannot be read accurately, and this will introduce a considerable uncertainty into the design.

An economic exchanger design cannot normally be achieved if the correction factor  $F_t$  falls below about 0.75. In these circumstances an alternative type of exchanger should be considered which gives a closer approach to true counter-current flow. The use of two or more shells in series, or multiple shell-side passes, will give a closer approach to true counter-current flow, and should be considered where a temperature cross is likely to occur.

Where both sensible and latent heat is transferred, it will be necessary to divide the temperature profile into sections and calculate the mean temperature difference for each section.

## 12.7. SHELL AND TUBE EXCHANGERS: GENERAL DESIGN CONSIDERATIONS

### 12.7.1. Fluid allocation: shell or tubes

Where no phase change occurs, the following factors will determine the allocation of the fluid streams to the shell or tubes.

*Corrosion.* The more corrosive fluid should be allocated to the tube-side. This will reduce the cost of expensive alloy or clad components.

*Fouling.* The fluid that has the greatest tendency to foul the heat-transfer surfaces should be placed in the tubes. This will give better control over the design fluid velocity, and the higher allowable velocity in the tubes will reduce fouling. Also, the tubes will be easier to clean.

*Fluid temperatures.* If the temperatures are high enough to require the use of special alloys placing the higher temperature fluid in the tubes will reduce the overall cost. At moderate temperatures, placing the hotter fluid in the tubes will reduce the shell surface temperatures, and hence the need for lagging to reduce heat loss, or for safety reasons.

*Operating pressures.* The higher pressure stream should be allocated to the tube-side. High-pressure tubes will be cheaper than a high-pressure shell.

*Pressure drop.* For the same pressure drop, higher heat-transfer coefficients will be obtained on the tube-side than the shell-side, and fluid with the lowest allowable pressure drop should be allocated to the tube-side.

*Viscosity.* Generally, a higher heat-transfer coefficient will be obtained by allocating the more viscous material to the shell-side, providing the flow is turbulent. The critical Reynolds number for turbulent flow in the shell is in the region of 200. If turbulent flow cannot be achieved in the shell it is better to place the fluid in the tubes, as the tube-side heat-transfer coefficient can be predicted with more certainty.

*Stream flow-rates.* Allocating the fluids with the lowest flow-rate to the shell-side will normally give the most economical design.

### 12.7.2. Shell and tube fluid velocities

High velocities will give high heat-transfer coefficients but also a high-pressure drop. The velocity must be high enough to prevent any suspended solids settling, but not so high as to cause erosion. High velocities will reduce fouling. Plastic inserts are sometimes used to reduce erosion at the tube inlet. Typical design velocities are given below:

#### **Liquids**

Tube-side, process fluids: 1 to 2 m/s, maximum 4 m/s if required to reduce fouling; water: 1.5 to 2.5 m/s.

Shell-side: 0.3 to 1 m/s.

#### **Vapours**

For vapours, the velocity used will depend on the operating pressure and fluid density; the lower values in the ranges given below will apply to high molecular weight materials.

Vacuum	50 to 70 m/s
Atmospheric pressure	10 to 30 m/s
High pressure	5 to 10 m/s

### 12.7.3. Stream temperatures

The closer the temperature approach used (the difference between the outlet temperature of one stream and the inlet temperature of the other stream) the larger will be the heat-transfer area required for a given duty. The optimum value will depend on the application, and can only be determined by making an economic analysis of alternative designs. As a general guide the greater temperature difference should be at least 20°C, and the least temperature difference 5 to 7°C for coolers using cooling water, and 3 to 5°C using refrigerated brines. The maximum temperature rise in recirculated cooling water is limited to around 30°C. Care should be taken to ensure that cooling media temperatures are kept well above the freezing point of the process materials. When the heat exchange is between process fluids for heat recovery the optimum approach temperatures will normally not be lower than 20°C.

### 12.7.4. Pressure drop

In many applications the pressure drop available to drive the fluids through the exchanger will be set by the process conditions, and the available pressure drop will vary from a few millibars in vacuum service to several bars in pressure systems.

When the designer is free to select the pressure drop an economic analysis can be made to determine the exchanger design which gives the lowest operating costs, taking into consideration both capital and pumping costs. However, a full economic analysis will only be justified for very large, expensive, exchangers. The values suggested below can be used as a general guide, and will normally give designs that are near the optimum.

#### *Liquids*

Viscosity	<1 mN s/m <sup>2</sup>	35 kN/m <sup>2</sup>
	1 to 10 mN s/m <sup>2</sup>	50–70 kN/m <sup>2</sup>

#### *Gas and vapours*

High vacuum	0.4–0.8 kN/m <sup>2</sup>
Medium vacuum	0.1 × absolute pressure
1 to 2 bar	0.5 × system gauge pressure
Above 10 bar	0.1 × system gauge pressure

When a high-pressure drop is utilised, care must be taken to ensure that the resulting high fluid velocity does not cause erosion or flow-induced tube vibration.

### 12.7.5. Fluid physical properties

The fluid physical properties required for heat-exchanger design are: density, viscosity, thermal conductivity and temperature-enthalpy correlations (specific and latent heats). Sources of physical property data are given in Chapter 8. The thermal conductivities of commonly used tube materials are given in Table 12.6.

Table 12.6. Conductivity of metals

Metal	Temperature (°C)	$k_w$ (W/m°C)
Aluminium	0	202
	100	206
Brass (70 Cu, 30 Zn)	0	97
	100	104
	400	116
Copper	0	388
	100	378
Nickel	0	62
	212	59
Cupro-nickel (10 per cent Ni)	0-100	45
Monel	0-100	30
Stainless steel (18/8)	0-100	16
	0	45
Steel	100	45
	600	36
	0-100	16
Titanium	0-100	16

In the correlations used to predict heat-transfer coefficients, the physical properties are usually evaluated at the mean stream temperature. This is satisfactory when the temperature change is small, but can cause a significant error when the change in temperature is large. In these circumstances, a simple, and safe, procedure is to evaluate the heat-transfer coefficients at the stream inlet and outlet temperatures and use the lowest of the two values. Alternatively, the method suggested by Frank (1978) can be used; in which equations 12.1 and 12.3 are combined:

$$Q = \frac{A[U_2(T_1 - t_2) - U_1(T_2 - t_1)]}{\ln \left[ \frac{U_2(T_1 - t_2)}{U_1(T_2 - t_1)} \right]} \quad (12.9)$$

where  $U_1$  and  $U_2$  are evaluated at the ends of the exchanger. Equation 12.9 is derived by assuming that the heat-transfer coefficient varies linearly with temperature.

If the variation in the physical properties is too large for these simple methods to be used it will be necessary to divide the temperature-enthalpy profile into sections and evaluate the heat-transfer coefficients and area required for each section.

## 12.8. TUBE-SIDE HEAT-TRANSFER COEFFICIENT AND PRESSURE DROP (SINGLE PHASE)

### 12.8.1. Heat transfer

#### *Turbulent flow*

Heat-transfer data for turbulent flow inside conduits of uniform cross-section are usually correlated by an equation of the form:

$$Nu = CR e^a Pr^b \left( \frac{\mu}{\mu_w} \right)^c \quad (12.10)$$

where  $Nu = \text{Nusselt number} = (h_i d_e / k_f)$ ,  
 $Re = \text{Reynolds number} = (\rho u_t d_e / \mu) = (G_t d_e / \mu)$ ,  
 $Pr = \text{Prandtl number} = (C_p \mu / k_f)$   
 and:  $h_i = \text{inside coefficient, W/m}^2\text{°C}$ ,  
 $d_e = \text{equivalent (or hydraulic mean) diameter, m}$

$$d_e = \frac{4 \times \text{cross-sectional area for flow}}{\text{wetted perimeter}} = d_i \text{ for tubes,}$$

$u_t = \text{fluid velocity, m/s}$ ,  
 $k_f = \text{fluid thermal conductivity, W/m}^2\text{°C}$ ,  
 $G_t = \text{mass velocity, mass flow per unit area, kg/m}^2\text{s}$ ,  
 $\mu = \text{fluid viscosity at the bulk fluid temperature, Ns/m}^2$ ,  
 $\mu_w = \text{fluid viscosity at the wall}$ ,  
 $C_p = \text{fluid specific heat, heat capacity, J/kg}^{\circ}\text{C}$ .

The index for the Reynolds number is generally taken as 0.8. That for the Prandtl number can range from 0.3 for cooling to 0.4 for heating. The index for the viscosity factor is normally taken as 0.14 for flow in tubes, from the work of Sieder and Tate (1936), but some workers report higher values. A general equation that can be used for exchanger design is:

$$Nu = C Re^{0.8} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.11)$$

where  $C = 0.021$  for gases,  
 $= 0.023$  for non-viscous liquids,  
 $= 0.027$  for viscous liquids.

It is not really possible to find values for the constant and indexes to cover the complete range of process fluids, from gases to viscous liquids, but the values predicted using equation 12.11 should be sufficiently accurate for design purposes. The uncertainty in the prediction of the shell-side coefficient and fouling factors will usually far outweigh any error in the tube-side value. Where a more accurate prediction than that given by equation 12.11 is required, and justified, the data and correlations given in the Engineering Science Data Unit reports are recommended: ESDU 92003 and 93018 (1998).

Butterworth (1977) gives the following equation, which is based on the ESDU work:

$$St = E Re^{-0.205} Pr^{-0.505} \quad (12.12)$$

where  $St = \text{Stanton number} = (Nu / Re Pr) = (h_i / \rho u_t C_p)$   
 and  $E = 0.0225 \exp(-0.0225 (\ln Pr)^2)$ .

Equation 12.12 is applicable at Reynolds numbers greater than 10,000.

### **Hydraulic mean diameter**

In some texts the equivalent (hydraulic mean) diameter is defined differently for use in calculating the heat transfer coefficient in a conduit or channel, than for calculating the pressure drop. The perimeter through which the heat is being transferred is used in place of the total wetted perimeter. In practice, the use of  $d_e$  calculated either way will make



little difference to the value of the estimated overall coefficient; as the film coefficient is only, roughly, proportional to  $d_e^{-0.2}$ .

It is the full wetted perimeter that determines the flow regime and the velocity gradients in a channel. So, in this book,  $d_e$  determined using the full wetted perimeter will be used for both pressure drop and heat transfer calculations. The actual area through which the heat is transferred should, of course, be used to determine the rate of heat transfer; equation 12.1.

### **Laminar flow**

Below a Reynolds number of about 2000 the flow in pipes will be laminar. Providing the natural convection effects are small, which will normally be so in forced convection, the following equation can be used to estimate the film heat-transfer coefficient:

$$Nu = 1.86(RePr)^{0.33} \left( \frac{d_e}{L} \right)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.13)$$

Where  $L$  is the length of the tube in metres.

If the Nusselt number given by equation 12.13 is less than 3.5, it should be taken as 3.5.

In laminar flow the length of the tube can have a marked effect on the heat-transfer rate for length to diameter ratios less than 500.

### **Transition region**

In the flow region between laminar and fully developed turbulent flow heat-transfer coefficients cannot be predicted with certainty, as the flow in this region is unstable, and the transition region should be avoided in exchanger design. If this is not practicable the coefficient should be evaluated using both equations 12.11 and 12.13 and the least value taken.

### **Heat-transfer factor, $j_h$**

It is often convenient to correlate heat-transfer data in terms of a heat transfer “ $j$ ” factor, which is similar to the friction factor used for pressure drop (see Volume 1, Chapters 3 and 9). The heat-transfer factor is defined by:

$$j_h = StPr^{0.67} \left( \frac{\mu}{\mu_w} \right)^{-0.14} \quad (12.14)$$

The use of the  $j_h$  factor enables data for laminar and turbulent flow to be represented on the same graph; Figure 12.23. The  $j_h$  values obtained from Figure 12.23 can be used with equation 12.14 to estimate the heat-transfer coefficients for heat-exchanger tubes and commercial pipes. The coefficient estimated for pipes will normally be conservative (on the high side) as pipes are rougher than the tubes used for heat exchangers, which are finished to closer tolerances. Equation 12.14 can be rearranged to a more convenient form:

$$\frac{h_i d_i}{k_f} = j_h RePr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.15)$$

*Note.* Kern (1950), and other workers, define the heat transfer factor as:

$$j_H = NuPr^{-1/3} \left( \frac{\mu}{\mu_w} \right)^{-0.14}$$

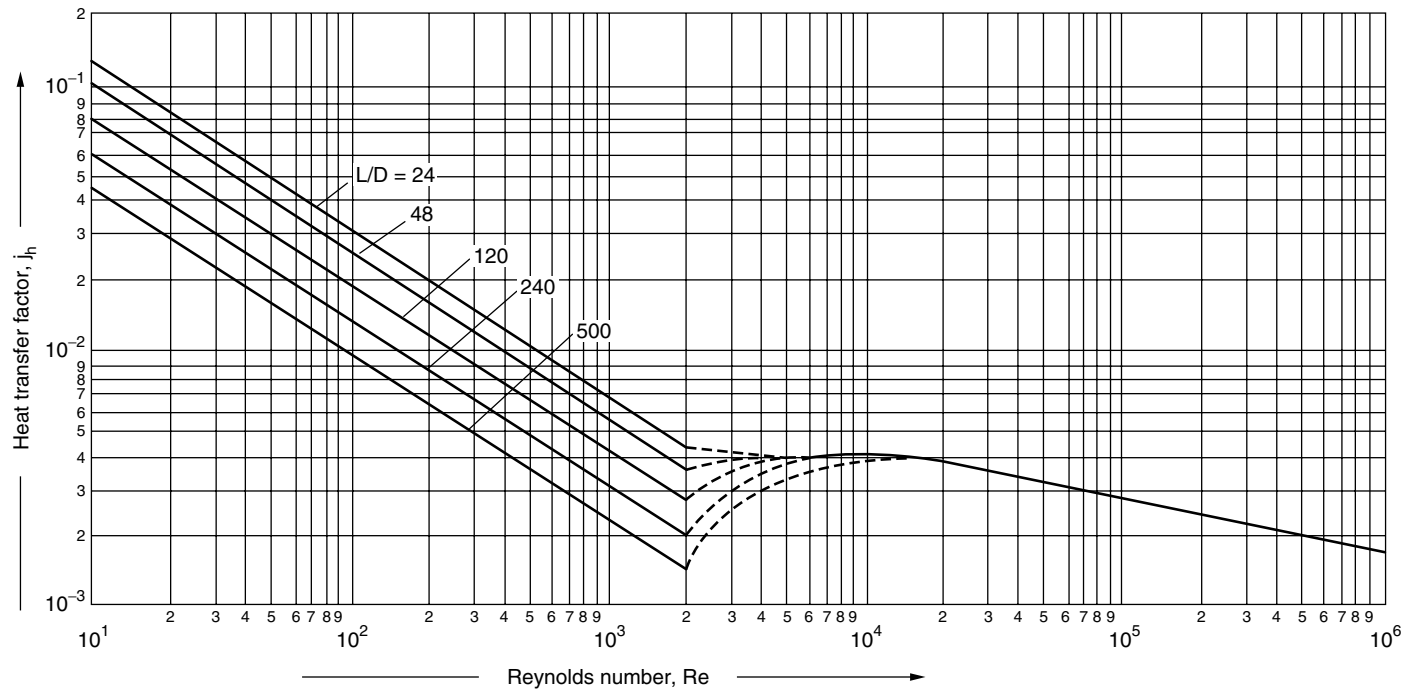


Figure 12.23. Tube-side heat-transfer factor

The relationship between  $j_h$  and  $j_H$  is given by:

$$j_H = j_h Re$$

### **Viscosity correction factor**

The viscosity correction factor will normally only be significant for viscous liquids.

To apply the correction an estimate of the wall temperature is needed. This can be made by first calculating the coefficient without the correction and using the following relationship to estimate the wall temperature:

$$h_i(t_w - t) = U(T - t) \quad (12.16)$$

where  $t$  = tube-side bulk temperature (mean),

$t_w$  = estimated wall temperature,

$T$  = shell-side bulk temperature (mean).

Usually an approximate estimate of the wall temperature is sufficient, but trial-and-error calculations can be made to obtain a better estimate if the correction is large.

### **Coefficients for water**

Though equations 12.11 and 12.13 and Figure 12.23 may be used for water, a more accurate estimate can be made by using equations developed specifically for water. The physical properties are conveniently incorporated into the correlation. The equation below has been adapted from data given by Eagle and Ferguson (1930):

$$h_i = \frac{4200(1.35 + 0.02t)u_t^{0.8}}{d_i^{0.2}} \quad (12.17)$$

where  $h_i$  = inside coefficient, for water,  $W/m^2\text{ }^\circ\text{C}$ ,

$t$  = water temperature,  $^\circ\text{C}$ ,

$u_t$  = water velocity, m/s,

$d_i$  = tube inside diameter, mm.

## **12.8.2. Tube-side pressure drop**

There are two major sources of pressure loss on the tube-side of a shell and tube exchanger: the friction loss in the tubes and the losses due to the sudden contraction and expansion and flow reversals that the fluid experiences in flow through the tube arrangement.

The tube friction loss can be calculated using the familiar equations for pressure-drop loss in pipes (see Volume 1, Chapter 3). The basic equation for isothermal flow in pipes (constant temperature) is:

$$\Delta P = 8j_f \left( \frac{L'}{d_i} \right) \frac{\rho u_t^2}{2} \quad (12.18)$$

where  $j_f$  is the dimensionless friction factor and  $L'$  is the effective pipe length.

The flow in a heat exchanger will clearly not be isothermal, and this is allowed for by including an empirical correction factor to account for the change in physical properties with temperature. Normally only the change in viscosity is considered:

$$\Delta P = 8j_f(L'/d_i)\rho\frac{u_t^2}{2}\left(\frac{\mu}{\mu_w}\right)^{-m} \quad (12.19)$$

$m = 0.25$  for laminar flow,  $Re < 2100$ ,  
 $= 0.14$  for turbulent flow,  $Re > 2100$ .

Values of  $j_f$  for heat exchanger tubes can be obtained from Figure 12.24; commercial pipes are given in Chapter 5.

The pressure losses due to contraction at the tube inlets, expansion at the exits, and flow reversal in the headers, can be a significant part of the total tube-side pressure drop. There is no entirely satisfactory method for estimating these losses. Kern (1950) suggests adding four velocity heads per pass. Frank (1978) considers this to be too high, and recommends 2.5 velocity heads. Butterworth (1978) suggests 1.8. Lord *et al.* (1970) take the loss per pass as equivalent to a length of tube equal to 300 tube diameters for straight tubes, and 200 for U-tubes; whereas Evans (1980) appears to add only 67 tube diameters per pass.

The loss in terms of velocity heads can be estimated by counting the number of flow contractions, expansions and reversals, and using the factors for pipe fittings to estimate the number of velocity heads lost. For two tube passes, there will be two contractions, two expansions and one flow reversal. The head loss for each of these effects (see Volume 1, Chapter 3) is: contraction 0.5, expansion 1.0, 180° bend 1.5; so for two passes the maximum loss will be

$$\begin{aligned} 2 \times 0.5 + 2 \times 1.0 + 1.5 &= 4.5 \text{ velocity heads} \\ &= \underline{\underline{2.25 \text{ per pass}}} \end{aligned}$$

From this, it appears that Frank's recommended value of 2.5 velocity heads per pass is the most realistic value to use.

Combining this factor with equation 12.19 gives

$$\Delta P_t = N_p \left[ 8j_f \left( \frac{L}{d_i} \right) \left( \frac{\mu}{\mu_w} \right)^{-m} + 2.5 \right] \frac{\rho u_t^2}{2} \quad (12.20)$$

where  $\Delta P_t$  = tube-side pressure drop, N/m<sup>2</sup> (Pa),

$N_p$  = number of tube-side passes,

$u_t$  = tube-side velocity, m/s,

$L$  = length of one tube.

Another source of pressure drop will be the flow expansion and contraction at the exchanger inlet and outlet nozzles. This can be estimated by adding one velocity head for the inlet and 0.5 for the outlet, based on the nozzle velocities.

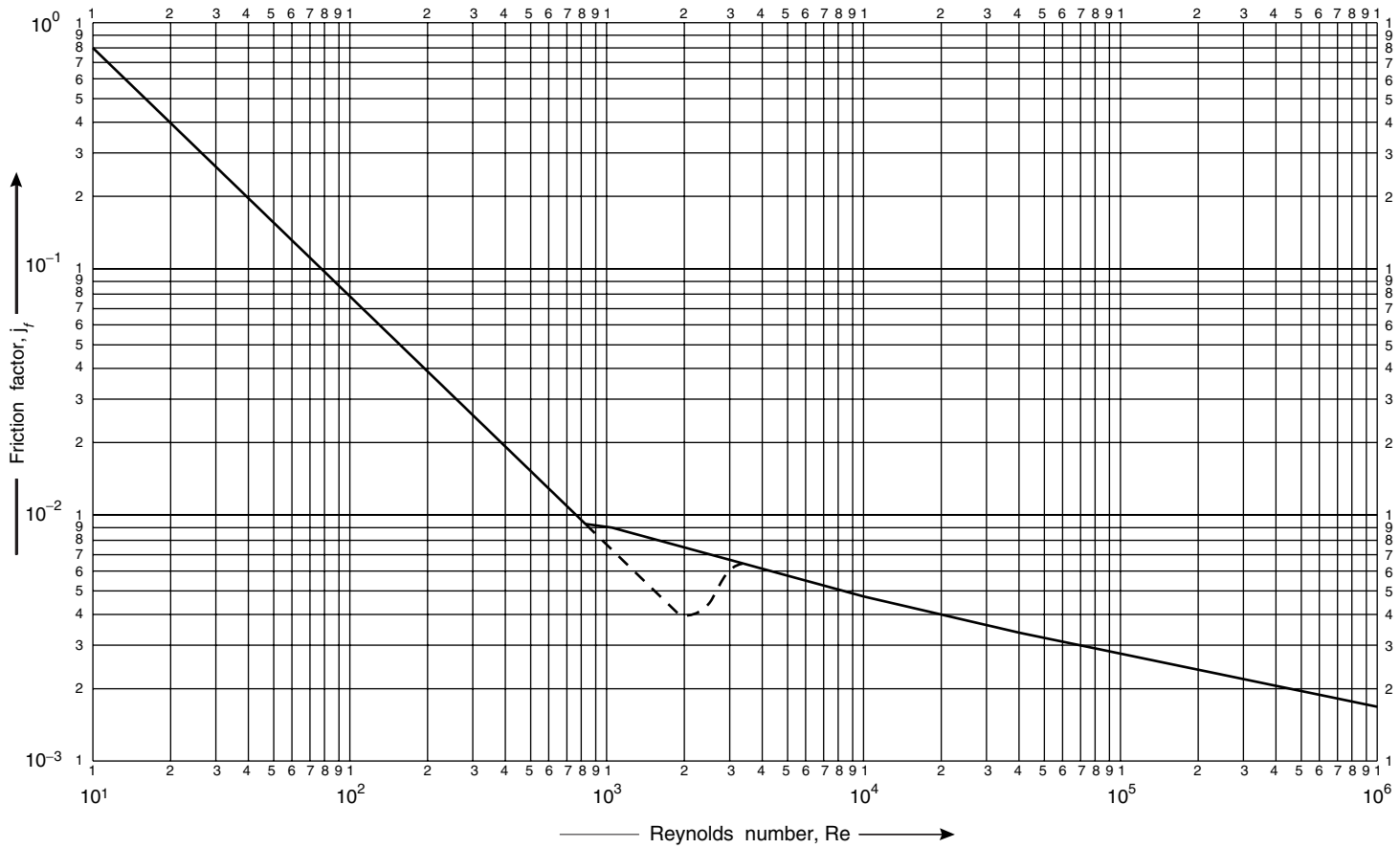


Figure 12.24. Tube-side friction factors

Note: The friction factor  $j_f$  is the same as the friction factor for pipes  $\phi (= (R/\rho u^2))$ , defined in Volume 1 Chapter 3.

## 12.9. SHELL-SIDE HEAT-TRANSFER AND PRESSURE DROP (SINGLE PHASE)

### 12.9.1. Flow pattern

The flow pattern in the shell of a segmentally baffled heat exchanger is complex, and this makes the prediction of the shell-side heat-transfer coefficient and pressure drop very much more difficult than for the tube-side. Though the baffles are installed to direct the flow across the tubes, the actual flow of the main stream of fluid will be a mixture of cross flow between the baffles, coupled with axial (parallel) flow in the baffle windows; as shown in Figure 12.25. Not all the fluid flow follows the path shown in Figure 12.25; some will leak through gaps formed by the clearances that have to be allowed for fabrication and assembly of the exchanger. These leakage and bypass streams are shown in Figure 12.26, which is based on the flow model proposed by Tinker (1951, 1958). In Figure 12.26, Tinker's nomenclature is used to identify the various streams, as follows:

Stream A is the tube-to-baffle leakage stream. The fluid flowing through the clearance between the tube outside diameter and the tube hole in the baffle.

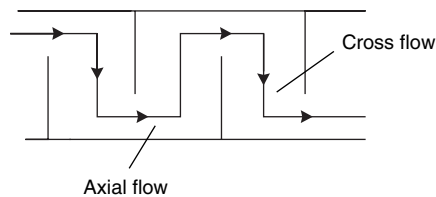


Figure 12.25. Idealised main stream flow

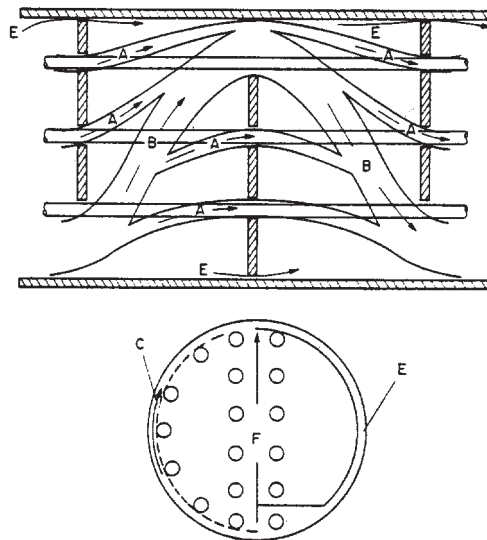


Figure 12.26. Shell-side leakage and by-pass paths

Stream B is the actual cross-flow stream.

Stream C is the bundle-to-shell bypass stream. The fluid flowing in the clearance area between the outer tubes in the bundle (bundle diameter) and the shell.

Stream E is the baffle-to-shell leakage stream. The fluid flowing through the clearance between the edge of a baffle and the shell wall.

Stream F is the pass-partition stream. The fluid flowing through the gap in the tube arrangement due to the pass partition plates. Where the gap is vertical it will provide a low-pressure drop path for fluid flow.

*Note.* There is no stream D.

The fluid in streams C, E and F bypasses the tubes, which reduces the effective heat-transfer area.

Stream C is the main bypass stream and will be particularly significant in pull-through bundle exchangers, where the clearance between the shell and bundle is of necessity large. Stream C can be considerably reduced by using sealing strips; horizontal strips that block the gap between the bundle and the shell, Figure 12.27. Dummy tubes are also sometimes used to block the pass-partition leakage stream F.

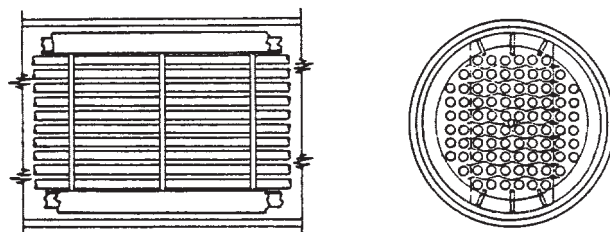


Figure 12.27. Sealing strips

The tube-to-baffle leakage stream A does not bypass the tubes, and its main effect is on pressure drop rather than heat transfer.

The clearances will tend to plug as the exchanger becomes fouled and this will increase the pressure drop; see Section 12.9.6.

### 12.9.2. Design methods

The complex flow pattern on the shell-side, and the great number of variables involved, make it difficult to predict the shell-side coefficient and pressure drop with complete assurance. In methods used for the design of exchangers prior to about 1960 no attempt was made to account for the leakage and bypass streams. Correlations were based on the total stream flow, and empirical methods were used to account for the performance of real exchangers compared with that for cross flow over ideal tube banks. Typical of these “bulk-flow” methods are those of Kern (1950) and Donohue (1955). Reliable predictions can only be achieved by comprehensive analysis of the contribution to heat transfer and pressure drop made by the individual streams shown in Figure 12.26. Tinker (1951, 1958) published the first detailed stream-analysis method for predicting shell-side heat-transfer coefficients and pressure drop, and the methods subsequently developed

have been based on his model. Tinker's presentation is difficult to follow, and his method difficult and tedious to apply in manual calculations. It has been simplified by Devore (1961, 1962); using standard tolerance for commercial exchangers and only a limited number of baffle cuts. Devore gives nomographs that facilitate the application of the method in manual calculations. Mueller (1973) has further simplified Devore's method and gives an illustrative example.

The Engineering Sciences Data Unit has also published a method for estimating shell-side the pressure drop and heat transfer coefficient, EDSU Design Guide 83038 (1984). The method is based on a simplification of Tinker's work. It can be used for hand calculations, but as iterative procedures are involved it is best programmed for use with personal computers.

Tinker's model has been used as the basis for the proprietary computer methods developed by Heat Transfer Research Incorporated; see Palen and Taborek (1969), and by Heat Transfer and Fluid Flow Services; see Grant (1973).

Bell (1960, 1963) developed a semi-analytical method based on work done in the cooperative research programme on shell and tube exchangers at the University of Delaware. His method accounts for the major bypass and leakage streams and is suitable for a manual calculation. Bell's method is outlined in Section 12.9.4 and illustrated in Example 12.3.

Though Kern's method does not take account of the bypass and leakage streams, it is simple to apply and is accurate enough for preliminary design calculations, and for designs where uncertainty in other design parameters is such that the use of more elaborate methods is not justified. Kern's method is given in Section 12.9.3 and is illustrated in Examples 12.1 and 12.3.

### 12.9.3. Kern's method

This method was based on experimental work on commercial exchangers with standard tolerances and will give a reasonably satisfactory prediction of the heat-transfer coefficient for standard designs. The prediction of pressure drop is less satisfactory, as pressure drop is more affected by leakage and bypassing than heat transfer. The shell-side heat transfer and friction factors are correlated in a similar manner to those for tube-side flow by using a hypothetical shell velocity and shell diameter. As the cross-sectional area for flow will vary across the shell diameter, the linear and mass velocities are based on the maximum area for cross-flow: that at the shell equator. The shell equivalent diameter is calculated using the flow area between the tubes taken in the axial direction (parallel to the tubes) and the wetted perimeter of the tubes; see Figure 12.28.

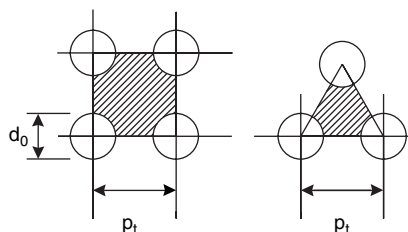


Figure 12.28. Equivalent diameter, cross-sectional areas and wetted perimeters



Shell-side  $j_h$  and  $j_f$  factors for use in this method are given in Figures 12.29 and 12.30, for various baffle cuts and tube arrangements. These figures are based on data given by Kern (1950) and by Ludwig (2001).

The procedure for calculating the shell-side heat-transfer coefficient and pressure drop for a single shell pass exchanger is given below:

### Procedure

1. Calculate the area for cross-flow  $A_s$  for the hypothetical row of tubes at the shell equator, given by:

$$A_s = \frac{(p_t - d_o)D_s l_B}{p_t} \quad (12.21)$$

where  $p_t$  = tube pitch,

$d_o$  = tube outside diameter,

$D_s$  = shell inside diameter, m,

$l_B$  = baffle spacing, m.

The term  $(p_t - d_o)/p_t$  is the ratio of the clearance between tubes and the total distance between tube centres.

2. Calculate the shell-side mass velocity  $G_s$  and the linear velocity  $u_s$ :

$$G_s = \frac{W_s}{A_s}$$

$$u_s = \frac{G_s}{\rho}$$

where  $W_s$  = fluid flow-rate on the shell-side, kg/s,

$\rho$  = shell-side fluid density, kg/m<sup>3</sup>.

3. Calculate the shell-side equivalent diameter (hydraulic diameter), Figure 12.28. For a square pitch arrangement:

$$d_e = \frac{4 \left( \frac{p_t^2 - \pi d_o^2}{4} \right)}{\pi d_o} = \frac{1.27}{d_o} (p_t^2 - 0.785 d_o^2) \quad (12.22)$$

For an equilateral triangular pitch arrangement:

$$d_e = \frac{4 \left( \frac{p_t}{2} \times 0.87 p_t - \frac{1}{2} \pi \frac{d_o^2}{4} \right)}{\frac{\pi d_o}{2}} = \frac{1.10}{d_o} (p_t^2 - 0.917 d_o^2) \quad (12.23)$$

where  $d_e$  = equivalent diameter, m.

4. Calculate the shell-side Reynolds number, given by:

$$Re = \frac{G_s d_e}{\mu} = \frac{u_s d_e \rho}{\mu} \quad (12.24)$$

5. For the calculated Reynolds number, read the value of  $j_h$  from Figure 12.29 for the selected baffle cut and tube arrangement, and calculate the shell-side heat transfer

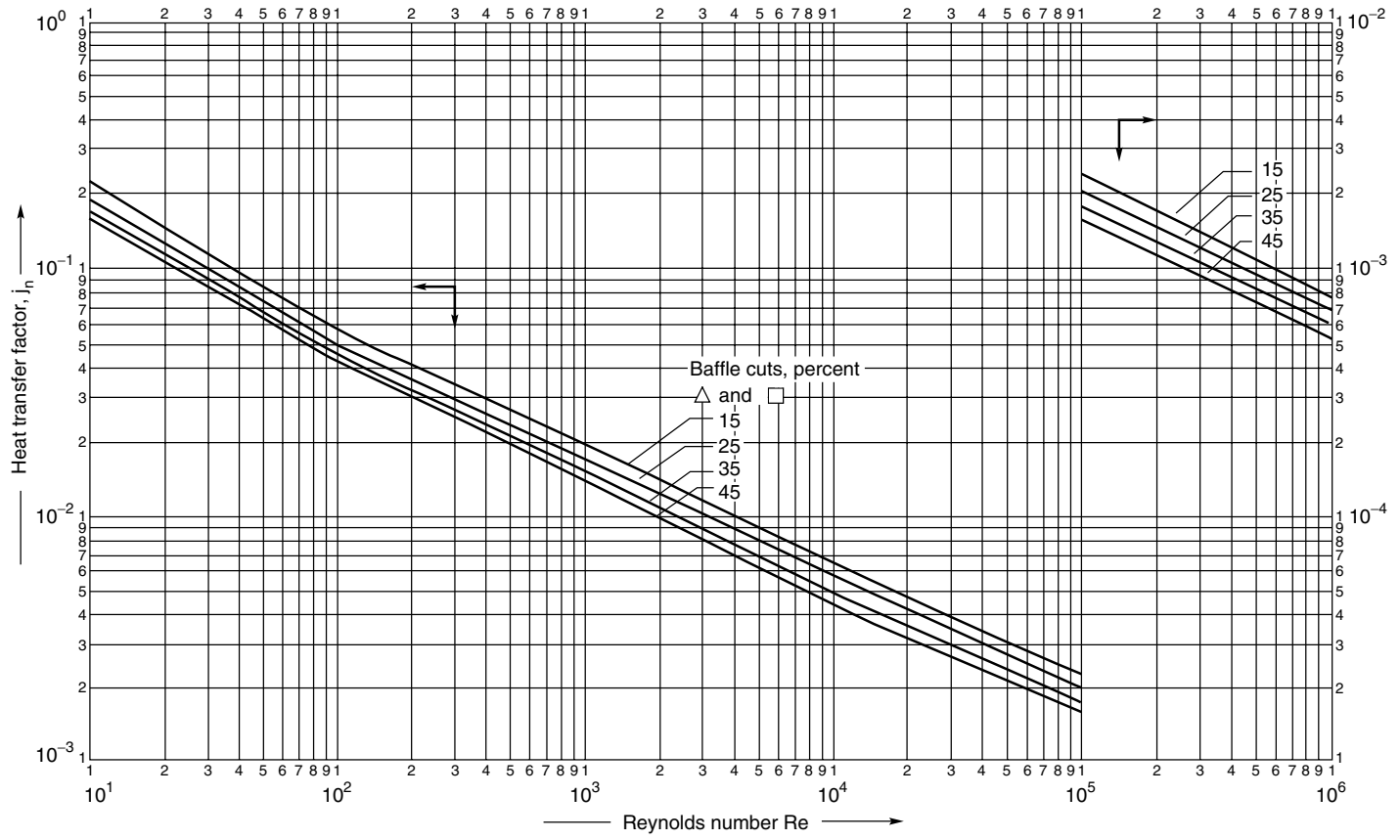


Figure 12.29. Shell-side heat-transfer factors, segmental baffles

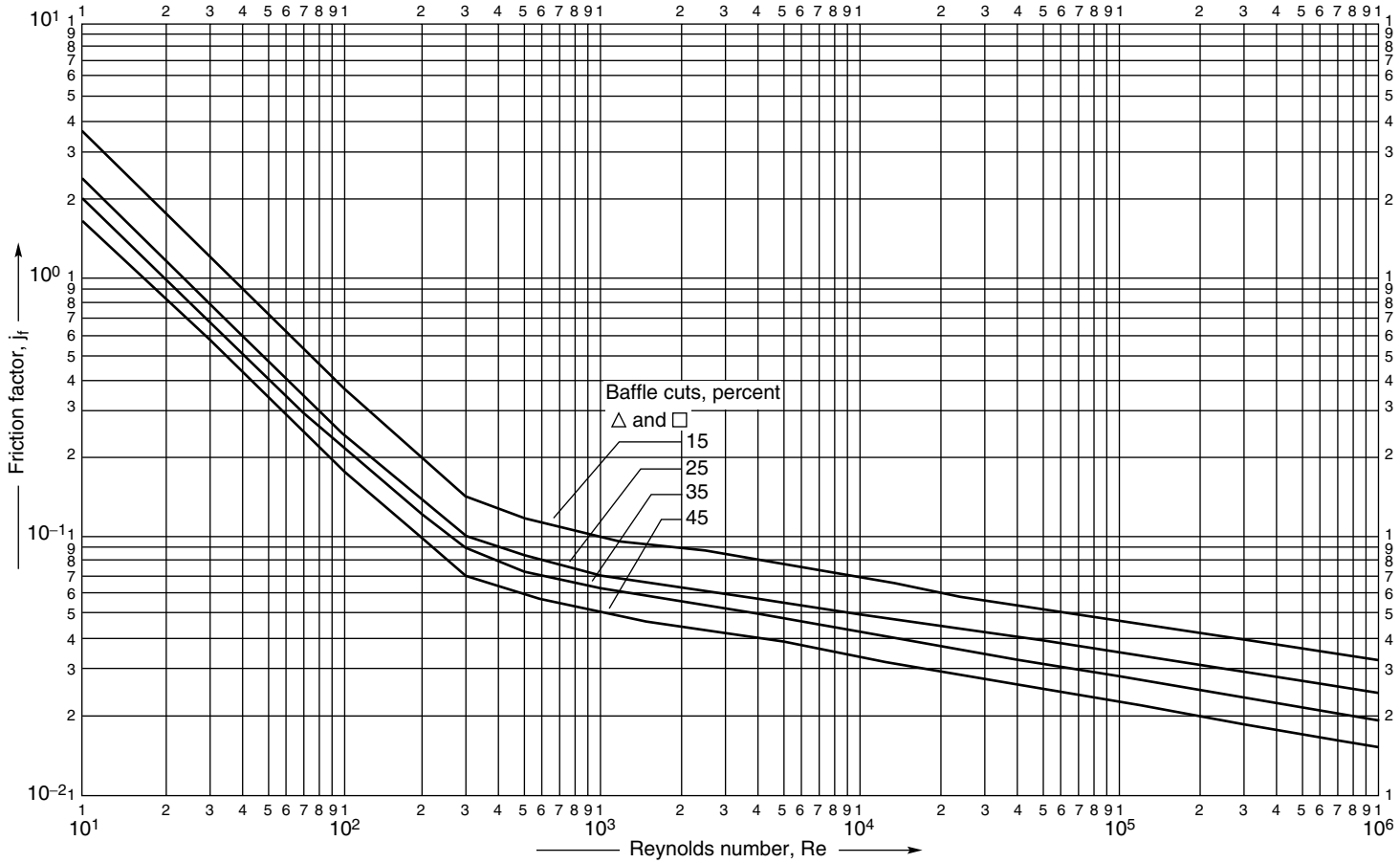


Figure 12.30. Shell-side friction factors, segmental baffles

coefficient  $h_s$  from:

$$Nu = \frac{h_s d_e}{k_f} = j_h Re Pr^{1/3} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.25)$$

The tube wall temperature can be estimated using the method given for the tube-side, Section 12.8.1.

6. For the calculated shell-side Reynolds number, read the friction factor from Figure 12.30 and calculate the shell-side pressure drop from:

$$\Delta P_s = 8 j_f \left( \frac{D_s}{d_e} \right) \left( \frac{L}{l_B} \right) \frac{\rho u_s^2}{2} \left( \frac{\mu}{\mu_w} \right)^{-0.14} \quad (12.26)$$

where  $L$  = tube length,

$l_B$  = baffle spacing.

The term  $(L/l_B)$  is the number of times the flow crosses the tube bundle =  $(N_b + 1)$ , where  $N_b$  is the number of baffles.

### Shell nozzle-pressure drop

The pressure loss in the shell nozzles will normally only be significant with gases. The nozzle pressure drop can be taken as equivalent to  $1\frac{1}{2}$  velocity heads for the inlet and  $\frac{1}{2}$  for the outlet, based on the nozzle area or the free area between the tubes in the row immediately adjacent to the nozzle, whichever is the least.

### Example 12.1

Design an exchanger to sub-cool condensate from a methanol condenser from 95°C to 40°C. Flow-rate of methanol 100,000 kg/h. Brackish water will be used as the coolant, with a temperature rise from 25° to 40°C.

### Solution

Only the thermal design will be considered.

This example illustrates Kern's method.

Coolant is corrosive, so assign to tube-side.

Heat capacity methanol = 2.84 kJ/kg°C

$$\text{Heat load} = \frac{100,000}{3600} \times 2.84(95 - 40) = 4340 \text{ kW}$$

Heat capacity water = 4.2 kJ/kg°C

$$\text{Cooling water flow} = \frac{4340}{4.2(40 - 25)} = 68.9 \text{ kg/s}$$

$$\Delta T_{lm} = \frac{(95 - 40) - (40 - 25)}{\ln \frac{(95 - 40)}{(40 - 25)}} = 31^\circ\text{C} \quad (12.4)$$

Use one shell pass and two tube passes

$$R = \frac{95 - 40}{40 - 25} = 3.67 \quad (12.6)$$

$$S = \frac{40 - 25}{95 - 25} = 0.21 \quad (12.7)$$

From Figure 12.19

$$F_t = 0.85$$

$$\Delta T_m = 0.85 \times 31 = 26^\circ\text{C}$$

From Figure 12.1

$$U = 600 \text{ W/m}^2\text{C}$$

Provisional area

$$A = \frac{4340 \times 10^3}{26 \times 600} = 278 \text{ m}^2 \quad (12.1)$$

Choose 20 mm o.d., 16 mm i.d., 4.88-m-long tubes ( $\frac{3}{4}$  in.  $\times$  16 ft), cupro-nickel.  
Allowing for tube-sheet thickness, take

$$L = 4.83 \text{ m}$$

$$\text{Area of one tube} = 4.83 \times 20 \times 10^{-3} \pi = 0.303 \text{ m}^2$$

$$\text{Number of tubes} = \frac{278}{0.303} = \underline{\underline{918}}$$

As the shell-side fluid is relatively clean use 1.25 triangular pitch.

$$\text{Bundle diameter } D_b = 20 \left( \frac{918}{0.249} \right)^{1/2.207} = 826 \text{ mm} \quad (12.3b)$$

Use a split-ring floating head type.

From Figure 12.10, bundle diametrical clearance = 68 mm,

$$\text{shell diameter, } D_s = 826 + 68 = 894 \text{ mm.}$$

(Note. nearest standard pipe sizes are 863.6 or 914.4 mm).

Shell size could be read from standard tube count tables.

### **Tube-side coefficient**

$$\text{Mean water temperature} = \frac{40 + 25}{2} = 33^\circ\text{C}$$

$$\text{Tube cross-sectional area} = \frac{\pi}{4} \times 16^2 = 201 \text{ mm}^2$$

$$\text{Tubes per pass} = \frac{918}{2} = 459$$

$$\text{Total flow area} = 459 \times 201 \times 10^{-6} = 0.092 \text{ m}^2$$

$$\text{Water mass velocity} = \frac{68.9}{0.092} = 749 \text{ kg/s m}^2$$

$$\text{Density water} = 995 \text{ kg/m}^3$$

$$\text{Water linear velocity} = \frac{749}{995} = 0.75 \text{ m/s}$$

$$h_i = \frac{4200(1.35 + 0.02 \times 33)0.75^{0.8}}{16^{0.2}} = 3852 \text{ W/m}^2\text{°C} \quad (12.17)$$

The coefficient can also be calculated using equation 12.15; this is done to illustrate use of this method.

$$\frac{h_i d_i}{k_f} = j_h Re Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14}$$

$$\text{Viscosity of water} = 0.8 \text{ mNs/m}^2$$

$$\text{Thermal conductivity} = 0.59 \text{ W/m}^\circ\text{C}$$

$$Re = \frac{\rho u d_i}{\mu} = \frac{995 \times 0.75 \times 16 \times 10^{-3}}{0.8 \times 10^{-3}} = 14,925$$

$$Pr = \frac{C_p \mu}{k_f} = \frac{4.2 \times 10^3 \times 0.8 \times 10^{-3}}{0.59} = 5.7$$

$$\text{Neglect } \left( \frac{\mu}{\mu_w} \right)$$

$$\frac{L}{d_i} = \frac{4.83 \times 10^3}{16} = 302$$

From Figure 12.23,  $j_h = 3.9 \times 10^{-3}$

$$h_i = \frac{0.59}{16 \times 10^{-3}} \times 3.9 \times 10^{-3} \times 14,925 \times 5.7^{0.33} = 3812 \text{ W/m}^2\text{°C}$$

Checks reasonably well with value calculated from equation 12.17; use lower figure.

### **Shell-side coefficient**

$$\text{Choose baffle spacing} = \frac{D_s}{5} = \frac{894}{5} = 178 \text{ mm.}$$

$$\text{Tube pitch} = 1.25 \times 20 = 25 \text{ mm}$$

$$\text{Cross-flow area } A_s = \frac{(25 - 20)}{25} 894 \times 178 \times 10^{-6} = 0.032 \text{ m}^2 \quad (12.21)$$

$$\text{Mass velocity, } G_s = \frac{100,000}{3600} \times \frac{1}{0.032} = 868 \text{ kg/s m}^2$$

$$\text{Equivalent diameter } d_e = \frac{1.1}{20} (25^2 - 0.917 \times 20^2) = 14.4 \text{ mm} \quad (12.23)$$

$$\text{Mean shell side temperature} = \frac{95 + 40}{2} = 68^\circ\text{C}$$

$$\text{Methanol density} = 750 \text{ kg/m}^3$$

$$\text{Viscosity} = 0.34 \text{ mNs/m}^2$$

$$\text{Heat capacity} = 2.84 \text{ kJ/kg}^\circ\text{C}$$

$$\text{Thermal conductivity} = 0.19 \text{ W/m}^\circ\text{C}$$

$$Re = \frac{G_s d_e}{\mu} = \frac{868 \times 14.4 \times 10^{-3}}{0.34 \times 10^{-3}} = 36,762 \quad (12.24)$$

$$Pr = \frac{C_p \mu}{k_f} = \frac{2.84 \times 10^3 \times 0.34 \times 10^{-3}}{0.19} = 5.1$$

Choose 25 per cent baffle cut, from Figure 12.29

$$j_h = 3.3 \times 10^{-3}$$

Without the viscosity correction term

$$h_s = \frac{0.19}{14.4 \times 10^{-3}} \times 3.3 \times 10^{-3} \times 36,762 \times 5.1^{1/3} = 2740 \text{ W/m}^2^\circ\text{C}$$

Estimate wall temperature

$$\text{Mean temperature difference} = 68 - 33 = 35^\circ\text{C}$$

across all resistances

$$\text{across methanol film} = \frac{U}{h_o} \times \Delta T = \frac{600}{2740} \times 35 = 8^\circ\text{C}$$

$$\text{Mean wall temperature} = 68 - 8 = 60^\circ\text{C}$$

$$\mu_w = 0.37 \text{ mNs/m}^2$$

$$\left(\frac{\mu}{\mu_w}\right)^{0.14} = 0.99$$

which shows that the correction for a low-viscosity fluid is not significant.

### Overall coefficient

Thermal conductivity of cupro-nickel alloys = 50 W/m<sup>°C</sup>.

Take the fouling coefficients from Table 12.2; methanol (light organic) 5000 Wm<sup>-2</sup>°C<sup>-1</sup>, brackish water (sea water), take as highest value, 3000 Wm<sup>-2</sup>°C<sup>-1</sup>

$$\begin{aligned} \frac{1}{U_o} &= \frac{1}{2740} + \frac{1}{5000} + \frac{20 \times 10^{-3} \ln\left(\frac{20}{16}\right)}{2 \times 50} \\ &\quad + \frac{20}{16} \times \frac{1}{3000} + \frac{20}{16} \times \frac{1}{3812} \end{aligned} \quad (12.2)$$

$$U_o = \underline{\underline{738 \text{ W/m}^2^\circ\text{C}}}$$

well above assumed value of 600 W/m<sup>2</sup>°C.

**Pressure drop****Tube-side**

From Figure 12.24, for  $Re = 14,925$

$$j_f = 4.3 \times 10^{-3}$$

Neglecting the viscosity correction term

$$\begin{aligned} \Delta P_t &= 2 \left( 8 \times 4.3 \times 10^{-3} \left( \frac{4.83 \times 10^3}{16} \right) + 2.5 \right) \frac{995 \times 0.75^2}{2} \quad (12.20) \\ &= 7211 \text{ N/m}^2 = 7.2 \text{ kPa (1.1 psi)} \end{aligned}$$

low, could consider increasing the number of tube passes.

**Shell side**

$$\text{Linear velocity} = \frac{G_s}{\rho} = \frac{868}{750} = 1.16 \text{ m/s}$$

From Figure 12.30, at  $Re = 36,762$

$$j_f = 4 \times 10^{-2}$$

Neglect viscosity correction

$$\begin{aligned} \Delta P_s &= 8 \times 4 \times 10^{-2} \left( \frac{894}{14.4} \right) \left( \frac{4.83 \times 10^3}{178} \right) \frac{750 \times 1.16^2}{2} \quad (12.26) \\ &= 272,019 \text{ N/m}^2 \\ &= 272 \text{ kPa (39 psi) too high,} \end{aligned}$$

could be reduced by increasing the baffle pitch. Doubling the pitch halves the shell-side velocity, which reduces the pressure drop by a factor of approximately  $(1/2)^2$

$$\Delta P_s = \frac{272}{4} = 68 \text{ kPa (10 psi), acceptable}$$

This will reduce the shell-side heat-transfer coefficient by a factor of  $(1/2)^{0.8}$  ( $h_o \propto Re^{0.8} \propto u_s^{0.8}$ )

$$h_o = 2740 \times \left(\frac{1}{2}\right)^{0.8} = 1573 \text{ W/m}^2\text{°C}$$

This gives an overall coefficient of  $615 \text{ W/m}^2\text{°C}$  – still above assumed value of  $600 \text{ W/m}^2\text{°C}$ .

**Example 12.2**

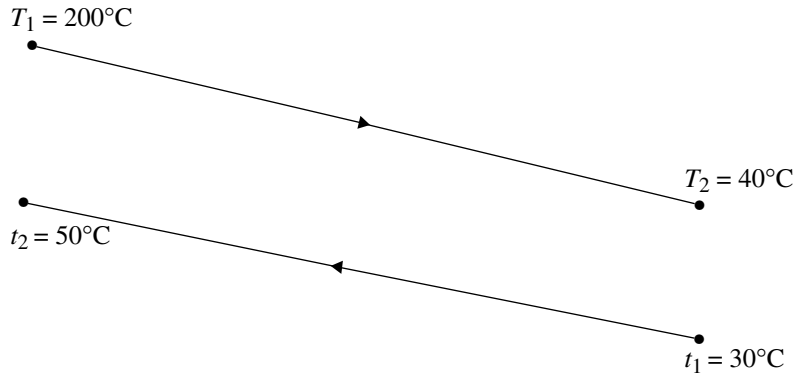
Gas oil at  $200^\circ\text{C}$  is to be cooled to  $40^\circ\text{C}$ . The oil flow-rate is  $22,500 \text{ kg/h}$ . Cooling water is available at  $30^\circ\text{C}$  and the temperature rise is to be limited to  $20^\circ\text{C}$ . The pressure drop allowance for each stream is  $100 \text{ kN/m}^2$ .

Design a suitable exchanger for this duty.



**Solution**

Only the thermal design will be carried out, to illustrate the calculation procedure for an exchanger with a divided shell.



$$\Delta T_{lm} = \frac{(200 - 40) - (40 - 30)}{\text{Ln} \frac{(200 - 50)}{(40 - 30)}} = 51.7^\circ\text{C} \quad (12.4)$$

$$R = (200 - 50)/(50 - 30) = 8.0 \quad (12.6)$$

$$S = (50 - 30)/(200 - 30) = 0.12 \quad (12.7)$$

These values do not intercept on the figure for a single shell-pass exchanger, Figure 12.19, so use the figure for a two-pass shell, Figure 12.20, which gives

$$F_t = 0.94, \text{ so}$$

$$\Delta T_m = 0.94 \times 51.7 = 48.6^\circ\text{C}$$

**Physical properties**

Water, from steam tables:

Temperature, °C	30	40	50
$C_p$ , kJ kg <sup>-1</sup> °C <sup>-1</sup>	4.18	4.18	4.18
$k$ , kWm <sup>-1</sup> °C <sup>-1</sup>	$618 \times 10^{-6}$	$631 \times 10^{-6}$	$643 \times 10^{-6}$
$\mu$ , mNm <sup>-2</sup> s	$797 \times 10^{-3}$	$671 \times 10^{-3}$	$544 \times 10^{-3}$
$\rho$ , kg m <sup>-3</sup>	995.2	992.8	990.1

Gas oil, from Kern, *Process Heat Transfer*, McGraw-Hill:

Temperature, °C	200	120	40
$C_p$ , kJ kg <sup>-1</sup> °C <sup>-1</sup>	2.59	2.28	1.97
$k$ , Wm <sup>-1</sup> °C <sup>-1</sup>	0.13	0.125	0.12
$\mu$ , mNm <sup>-2</sup> s	0.06	0.17	0.28
$\rho$ , kg m <sup>-3</sup>	830	850	870

*Duty:*

$$\text{Oil flow-rate} = 22,500/3600 = 6.25 \text{ kg/s}$$

$$Q = 6.25 \times 2.28 \times (200 - 40) = 2280 \text{ kW}$$

$$\text{Water flow-rate} = \frac{2280}{4.18(50 - 30)} = 27.27 \text{ kg/h}$$

From Figure 12.1, for cooling tower water and heavy organic liquid, take

$$U = 500 \text{ Wm}^{-2}\text{C}^{-1}$$

$$\text{Area required} = \frac{2280 \times 10^3}{500 \times 48.6} = 94 \text{ m}^2$$

### **Tube-side coefficient**

Select 20 mm o.d., 16 mm i.d. tubes, 4 m long, triangular pitch  $1.25d_o$ , carbon steel.

$$\text{Surface area of one tube} = \pi \times 20 \times 10^{-3} \times 4 = 0.251 \text{ m}^2$$

$$\text{Number of tubes required} = 94/0.251 = 375, \text{ say } 376, \text{ even number}$$

$$\text{Cross-sectional area, one tube} = \frac{\pi}{4} (16 \times 10^{-3})^2 = 2.011 \times 10^{-4} \text{ m}^2$$

$$\text{Total tube area} = 376 \times 2.011 \times 10^{-4} = 0.0756 \text{ m}^2$$

Put water through tube for ease of cleaning.

$$\text{Tube velocity, one pass} = 27.27/(992.8 \times 0.0756) = 0.363 \text{ m/s}$$

Too low to make effective use of the allowable pressure drop, try 4 passes.

$$u_t = 4 \times 0.363 = 1.45 \text{ m/s}$$

A floating head will be needed due to the temperature difference. Use a pull through type.

Tube-side heat transfer coefficient

$$h_i = \frac{4200(1.35 + 0.02 \times 40)1.45^{0.8}}{16^{0.2}} = 6982 \text{ Wm}^{-2}\text{C}^{-1} \quad (12.17)$$

### **Shell-side coefficient**

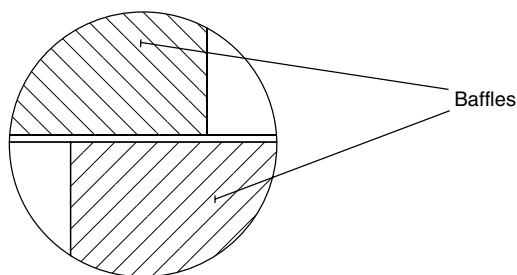
From Table 12.4 and equation 12.3*b*, for 4 passes,  $1.25d_o$  triangular pitch

$$\text{Bundle diameter, } D_b = 20(376/0.175)^{1/2.285} = 575 \text{ mm}$$

From Figure 12.10, for pull through head, clearance = 92 mm

$$\text{Shell diameter, } D_s = 575 + 92 = 667 \text{ mm (26 in pipe)}$$

Use 25 per cent cut baffles, baffle arrangement for divided shell as shown below:



Take baffle spacing as 1/5 shell diameter =  $667/5 = 133$  mm

Tube pitch,  $p_t = 1.25 \times 20 = 25$  mm

Area for flow,  $A_s$ , will be half that given by equation 12.21

$$A_s = 0.5 \times \left( \frac{25 - 20}{25} \times 0.667 \times 0.133 \right) = 0.00887 \text{ m}^2$$

$$G_s = 6.25/0.00887 = 704.6 \text{ kg/s}$$

$$u_s = 704.6/850 = 0.83 \text{ m/s, looks reasonable}$$

$$d_e = \frac{1.10}{20} (25^2 - 0.917 \times 20^2) = 14.2 \text{ mm} \quad (12.23)$$

$$\text{Re} = \frac{0.83 \times 14.2 \times 10^{-3} \times 850}{0.17 \times 10^{-3}} = 58,930$$

From Figure 12.29,  $j_h = 2.6 \times 10^{-3}$

$$\text{Pr} = (2.28 \times 10^3 \times 0.17 \times 10^{-3})/0.125 = 3.1$$

$$\text{Nu} = 2.6 \times 10^{-3} \times 58,930 \times 3.1^{1/3} = 223.4 \quad (12.25)$$

$$h_s = (223.4 \times 0.125)/(14.2 \times 10^{-3}) = 1967 \text{ Wm}^{-2}\text{C}^{-1}$$

### Overall coefficient

Take fouling factors as 0.00025 for cooling tower water and 0.0002 for gas oil (light organic). Thermal conductivity for carbon steel tubes  $45 \text{ Wm}^{-1}\text{C}^{-1}$ .

$$1/U_o = 1/1967 + 0.0002 + \frac{20 \times 10^{-3} \ln(20/16)}{2 \times 45}$$

$$+ 20/16(1/6982 + 0.00025) = 0.00125$$

$$U_o = 1/0.00125 = 800 \text{ Wm}^{-2}\text{C}^{-1} \quad (12.2)$$

Well above the initial estimate of  $500 \text{ Wm}^{-2}\text{C}^{-1}$ , so design has adequate area for the duty required.

### Pressure drops

#### Tube-side

$$\text{Re} = \frac{1.45 \times 16 \times 10^{-3} \times 992.8}{670 \times 10^{-6}} = 34,378 \quad (3.4 \times 10^4)$$

From Figure 12.24,  $j_f = 3.5 \times 10^{-3}$ . Neglecting the viscosity correction

$$\Delta P_t = 4 \left[ 8 \times 3.5 \times 10^{-3} \times \left( \frac{4}{16 \times 10^{-3}} \right) + 2.5 \right] 992.8 \times \frac{1.45^2}{2} = 39,660$$

$$= 40 \text{ kN/m}^2 \quad (12.20)$$

Well within the specification, so no need to check the nozzle pressure drop.

**Shell-side**

From Figure 12.30, for  $Re = 58,930$ ,  $j_s = 3.8 \times 10^{-2}$

With a divided shell, the path length  $= 2 \times (L/l_b)$

Neglecting the viscosity correction factor,

$$\begin{aligned} \Delta P_s &= 8 \times 3.8 \times 10^{-2} \left( \frac{662 \times 10^{-3}}{14.2 \times 10^{-3}} \right) \times \left( \frac{2 \times 4}{132 \times 10^{-3}} \right) \times 850 \times \frac{0.83^2}{2} = 251,481 \\ &= 252 \text{ kN/m}^2 \end{aligned} \quad (12.26)$$

Well within the specification, no need to check nozzle pressure drops.

So the proposed thermal design is satisfactory. As the calculated pressure drops are below that allowed, there is some scope for improving the design.

**Example 12.3**

Design a shell-and-tube exchanger for the following duty.

20,000 kg/h of kerosene (42° API) leaves the base of a kerosene side-stripping column at 200°C and is to be cooled to 90°C by exchange with 70,000 kg/h light crude oil (34° API) coming from storage at 40°C. The kerosene enters the exchanger at a pressure of 5 bar and the crude oil at 6.5 bar. A pressure drop of 0.8 bar is permissible on both streams. Allowance should be made for fouling by including a fouling factor of  $0.0003 \text{ (W/m}^2\text{°C)}^{-1}$  on the crude stream and  $0.0002 \text{ (W/m}^2\text{°C)}^{-1}$  on the kerosene stream.

**Solution**

The solution to this example illustrates the iterative nature of heat exchanger design calculations. An algorithm for the design of shell-and-tube exchangers is shown in Figure A (see p. 684). The procedure set out in this figure will be followed in the solution.

**Step 1: Specification**

The specification is given in the problem statement.

20,000 kg/h of kerosene (42° API) at 200°C cooled to 90°C, by exchange with 70,000 kg/h light crude oil (34° API) at 40°C.

The kerosene pressure 5 bar, the crude oil pressure 6.5 bar.

Permissible pressure drop of 0.8 bar on both streams.

Fouling factors: crude stream  $0.00035 \text{ (W/m}^2\text{°C)}^{-1}$ , kerosene stream  $0.0002 \text{ (W/m}^2\text{°C)}^{-1}$ .

To complete the specification, the duty (heat transfer rate) and the outlet temperature of the crude oil needed to be calculated.

The mean temperature of the kerosene  $= (200 + 90)/2 = 145^\circ\text{C}$ .

At this temperature the specific heat capacity of 42° API kerosene is  $2.47 \text{ kJ/kg}^\circ\text{C}$  (physical properties from D. Q. Kern, Process Heat Transfer, McGraw-Hill).

$$\text{Duty} = \frac{20,000}{3600} \times 2.47(200 - 90) = 1509.4 \text{ kW}$$

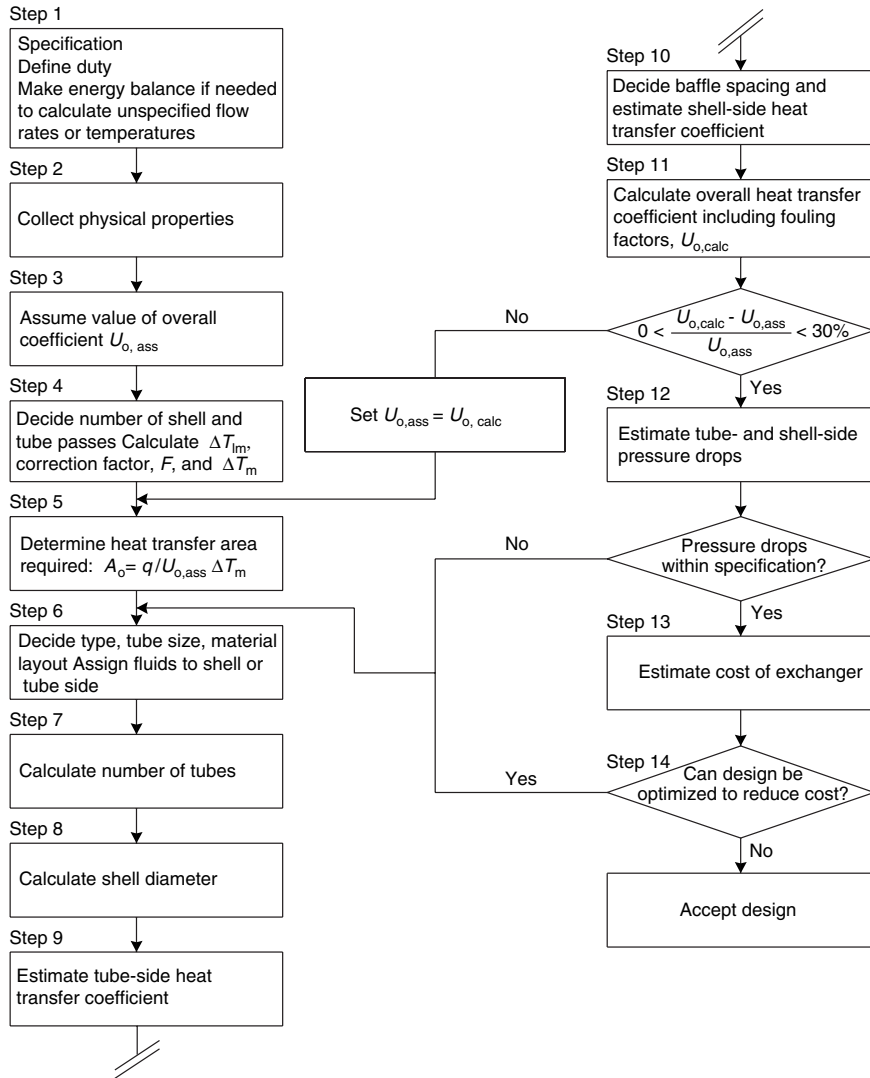


Figure A. Design procedure for shell-and-tube heat exchangers  
 Example 12.2 and Figure A were developed by the author for the Open University Course T333 *Principles and Applications of Heat Transfer*. They are reproduced here by permission of the Open University.

As a first trial take the mean temperature of the crude oil as equal to the inlet temperature, 40°C; specific heat capacity at this temperature = 2.01 kJ/kg°C.

An energy balance gives:

$$\frac{7000}{3600} \times 2.01(t_2 - 40) = 1509.4$$

$t_2 = 78.6^\circ\text{C}$  and the stream mean temperature =  $(40 + 78.6)/2 = 59.3^\circ\text{C}$ .

The specific heat at this temperature is 2.05 kJ/kg°C. A second trial calculation using this value gives  $t_2 = 77.9^\circ\text{C}$  and a new mean temperature of  $58.9^\circ\text{C}$ . There is no significant change in the specific heat at this mean temperature from the value used, so take the crude stream outlet temperature to be  $77.9^\circ\text{C}$ , say  $78^\circ\text{C}$ .

### Step 2: Physical Properties

<i>Kerosene</i>	inlet	mean	outlet	
temperature	200	145	90	°C
specific heat	2.72	2.47	2.26	kJ/kg°C
thermal conductivity	0.130	0.132	0.135	W/m°C
density	690	730	770	kg/m <sup>3</sup>
viscosity	0.22	0.43	0.80	mN sm <sup>-2</sup>
<i>Crude oil</i>	outlet	mean	inlet	
temperature	78	59	40	°C
specific heat	2.09	2.05	2.01	kJ/kg°C
thermal conductivity	0.133	0.134	0.135	W/m°C
density	800	820	840	kg/m <sup>3</sup>
viscosity	2.4	3.2	4.3	mN sm <sup>-2</sup>

### Step 3: Overall coefficient

For an exchanger of this type the overall coefficient will be in the range 300 to 500 W/m<sup>2</sup>°C, see Figure 12.1 and Table 12.1; so start with 300 W/m<sup>2</sup>°C.

### Step 4: Exchanger type and dimensions

An even number of tube passes is usually the preferred arrangement, as this positions the inlet and outlet nozzles at the same end of the exchanger, which simplifies the pipework.

Start with one shell pass and 2 tube passes.

$$\Delta T_{lm} = \frac{(200 - 78) - (90 - 40)}{\ln \frac{(200 - 78)}{(90 - 40)}} = 80.7^\circ\text{C} \quad (12.4)$$

$$R = \frac{(200 - 90)}{(78 - 40)} = 2.9 \quad (12.6)$$

$$S = \frac{(78 - 40)}{(200 - 40)} = 0.24 \quad (12.7)$$

From Figure 12.19,  $F_t = 0.88$ , which is acceptable.

So,  $\Delta T_m = 0.88 \times 80.7 = 71.0^\circ\text{C}$

**Step 5: Heat transfer area**

$$A_o = \frac{1509.4 \times 10^3}{300 \times 71.0} = 70.86 \text{ m}^2 \quad (12.1)$$

**Step 6: Layout and tube size**

Using a split-ring floating head exchanger for efficiency and ease of cleaning.

Neither fluid is corrosive, and the operating pressure is not high, so a plain carbon steel can be used for the shell and tubes.

The crude is dirtier than the kerosene, so put the crude through the tubes and the kerosene in the shell.

Use 19.05 mm (3/4 inch) outside diameter, 14.83 mm inside diameter, 5 m Long tubes (a popular size) on a triangular 23.81 mm pitch (pitch/dia. = 1.25).

**Step 7: Number of tubes**

Area of one tube (neglecting thickness of tube sheets)

$$= \pi \times 19.05 \times 10^{-3} \times 5 = 0.2992 \text{ m}^2$$

Number of tubes =  $70.89/0.2992 = 237$ , say 240

So, for 2 passes, tubes per pass = 120

Check the tube-side velocity at this stage to see if it looks reasonable.

$$\text{Tube cross-sectional area} = \frac{\pi}{4}(14.83 \times 10^{-3})^2 = 0.0001727 \text{ m}^2$$

$$\text{So area per pass} = 120 \times 0.0001727 = 0.02073 \text{ m}^2$$

$$\text{Volumetric flow} = \frac{70,000}{3600} \times \frac{1}{820} = 0.0237 \text{ m}^3/\text{s}$$

$$\text{Tube-side velocity, } u_t = \frac{0.0237}{0.02073} = 1.14 \text{ m/s}$$

The velocity is satisfactory, between 1 to 2 m/s, but may be a little low. This will show up when the pressure drop is calculated.

**Step 8: Bundle and shell diameter**

From Table 12.4, for 2 tube passes,  $K_1 = 0.249$ ,  $n_1 = 2.207$ ,

$$\text{so, } D_b = 19.05 \left( \frac{240}{0.249} \right)^{1/2.207} = 428 \text{ mm (0.43 m)} \quad (12.3b)$$

For a split-ring floating head exchanger the typical shell clearance from Figure 12.10 is 56 mm, so the shell inside diameter,

$$D_s = 428 + 56 = 484 \text{ mm}$$

**Step 9: Tube-side heat transfer coefficient**

$$Re = \frac{820 \times 1.14 \times 14.83 \times 10^{-3}}{3.2 \times 10^{-3}} = 4332, (4.3 \times 10^3)$$

$$Pr = \frac{2.05 \times 10^3 \times 3.2 \times 10^{-3}}{0.134} = 48.96$$

$$\frac{L}{d_i} = \frac{5000}{14.83} = 337$$

From Figure 12.23,  $j_h = 3.2 \times 10^{-3}$

$$Nu = 3.2 \times 10^{-3} (4332)(48.96)^{0.33} = 50.06 \quad (12.15)$$

$$h_i = 50.06 \times \left( \frac{0.134}{14.83 \times 10^{-3}} \right) = 452 \text{ W/m}^2\text{°C}$$

This is clearly too low if  $U_o$  is to be 300 W/m<sup>2</sup>°C. The tube-side velocity did look low, so increase the number of tube passes to 4. This will halve the cross-sectional area in each pass and double the velocity.

New  $u_t = 2 \times 1.14 = 2.3 \text{ m/s}$

and  $Re = 2 \times 4332 = 8664 (8.7 \times 10^3)$

$$j_h = 3.8 \times 10^{-3}$$

$$h_i = \left( \frac{0.134}{14.83 \times 10^{-3}} \right) \times 3.8 \times 10^{-3} (8664)(48.96)^{0.33} \\ = 1074 \text{ W/m}^2\text{°C}$$

**Step 10: Shell-side heat transfer coefficient**

Kern's method will be used.

With 4 tube passes the shell diameter will be larger than that calculated for 2 passes. For 4 passes  $K_1 = 0.175$  and  $n_1 = 2.285$ .

$$D_b = 19.05 \left( \frac{240}{0.175} \right)^{1/2.285} = 450 \text{ mm}, (0.45 \text{ m}) \quad (12.3b)$$

The bundle to shell clearance is still around 56 mm, giving:

$$D_s = 506 \text{ mm (about 20 inches)}$$

As a first trial take the baffle spacing =  $D_s/5$ , say 100 mm. This spacing should give good heat transfer without too high a pressure drop.

$$A_s = \frac{(23.81 - 19.05)}{23.81} 506 \times 100 = 10,116 \text{ mm}^2 = 0.01012 \text{ m}^2 \quad (12.21)$$

$$d_e = \frac{1.10}{19.05} (23.81^2 - 0.917 \times 19.05^2) = 13.52 \text{ mm} \quad (12.23)$$

$$\text{Volumetric flow-rate on shell-side} = \frac{20,000}{3600} \times \frac{1}{730} = 0.0076 \text{ m}^3/\text{s}$$



$$\text{Shell-side velocity} = \frac{0.076}{0.01012} = 0.75 \text{ m/s}$$

$$Re = \frac{730 \times 0.75 \times 13.52 \times 10^{-3}}{0.43 \times 10^{-3}} = 17,214, (1.72 \times 10^4)$$

$$Pr = \frac{2.47 \times 10^3 \times 0.43 \times 10^{-3}}{0.132} = 8.05$$

Use segmental baffles with a 25% cut. This should give a reasonable heat transfer coefficient without too large a pressure drop.

From Figure 12.29,  $j_h = 4.52 \times 10^{-3}$ .

Neglecting the viscosity correction:

$$h_s = \left( \frac{0.132}{13.52} \times 10^3 \right) \times 4.52 \times 10^{-3} \times 17,214 \times 8.05^{0.33} = 1505 \text{ W/m}^2\text{°C} \quad (12.25)$$

### Step 11: Overall coefficient

$$\frac{1}{U_o} = \left( \frac{1}{1074} + 0.00035 \right) \frac{19.05}{14.83} + \frac{19.05 \times 10^{-3} \text{Ln} \left( \frac{19.05}{14.83} \right)}{2 \times 55} + \frac{1}{1505} + 0.0002$$

$$U_o = 386 \text{ W/m}^2\text{°C} \quad (12.2)$$

This is above the initial estimate of 300 W/m<sup>2</sup>°C. The number of tubes could possibly be reduced, but first check the pressure drops.

### Step 12: Pressure drop

#### Tube-side

240 tubes, 4 passes, tube i.d. 14.83 mm,  $u_t$  2.3 m/s,  
 $Re = 8.7 \times 10^3$ . From Figure 12.24,  $j_f = 5 \times 10^{-3}$ .

$$\begin{aligned} \Delta P_t &= 4 \left( 8 \times 5 \times 10^{-3} \left( \frac{5000}{14.83} \right) + 2.5 \right) \frac{(820 \times 2.3^2)}{2} \\ &= 4(13.5 + 2.5) \frac{(820 \times 2.3^2)}{2} \\ &= 138,810 \text{ N/m}^2, 1.4 \text{ bar} \end{aligned} \quad (12.20)$$

This exceeds the specification. Return to step 6 and modify the design.

### Modified design

The tube velocity needs to be reduced. This will reduce the heat transfer coefficient, so the number of tubes must be increased to compensate. There will be a pressure drop across the inlet and outlet nozzles. Allow 0.1 bar for this, a typical figure (about 15% of the total); which leaves 0.7 bar across the tubes. Pressure drop is roughly proportional

to the square of the velocity and  $u_t$  is proportional to the number of tubes per pass. So the pressure drop calculated for 240 tubes can be used to estimate the number of tubes required.

$$\text{Tubes needed} = 240 / (0.6/1.4)^{0.5} = 365$$

Say, 360 with 4 passes.

Retain 4 passes as the heat transfer coefficient will be too low with 2 passes.

Second trial design: 360 tubes 19.05 mm o.d., 14.83 mm i.d., 5 m long, triangular pitch 23.81 mm.

$$D_b = 19.05 \left( \frac{360}{0.175} \right)^{1/2.285} = 537 \text{ mm}, (0.54 \text{ m}) \quad (12.3b)$$

From Figure 12.10 clearance with this bundle diameter = 59 mm

$$D_s = 537 + 59 = 596 \text{ mm}$$

$$\text{Cross-sectional area per pass} = \frac{360}{4} (14.83 \times 10^{-3})^2 \frac{\pi}{4} = 0.01555 \text{ m}^2$$

$$\text{Tube velocity } u_t = \frac{0.0237}{0.01555} = 1.524 \text{ m/s}$$

$$Re = \frac{820 \times 1.524 \times 14.83 \times 10^{-3}}{3.2 \times 10^{-3}} = 5792$$

$L/d$  is the same as the first trial, 337

$$j_h = 3.6 \times 10^{-3}$$

$$h_i = \left( \frac{0.134}{14.83} \times 10^{-3} \right) 3.6 \times 10^{-3} \times 5792 \times 48.96^{0.33} = 680 \text{ W/m}^2\text{°C} \quad (12.15)$$

This looks satisfactory, but check the pressure drop before doing the shell-side calculation.

$$j_f = 5.5 \times 10^{-3}$$

$$\Delta P_t = 4 \left( 8 \times 5.5 \times 10^{-3} \left( \frac{5000}{14.83} \right) + 2.5 \right) \frac{(820 \times 1.524^2)}{2} = 66,029 \text{ N/m}^2, 0.66 \text{ bar} \quad (12.20)$$

Well within specification.

Keep the same baffle cut and spacing.

$$A_s = \frac{(23.81 - 19.05)}{23.81} 596 \times 100 = 11,915 \text{ mm}^2, 0.01192 \text{ m}^2 \quad (12.21)$$

$$u_s = \frac{0.0076}{0.01192} = 0.638 \text{ m/s}$$

$$d_e = 13.52 \text{ mm}, \text{ as before}$$

$$Re = \frac{730 \times 0.638 \times 13.52 \times 10^{-3}}{0.43 \times 10^{-3}} = 14,644, (1.5 \times 10^4)$$

$$Pr = 8.05$$

$$j_h = 4.8 \times 10^{-3}, \quad j_f = 4.6 \times 10^{-2}$$

$$h_s = \left( \frac{0.132}{13.52 \times 10^{-3}} \right) 4.8 \times 10^{-3} \times 14,644 \times (8.05)^{0.33} = 1366 \text{ W/m}^2\text{°C}, \text{ looks OK} \quad (12.25)$$

$$\Delta P_s = 8 \times 4.6 \times 10^{-2} \left( \frac{596}{13.52} \right) \left( \frac{5000}{100} \right) \frac{(730 \times 0.638^2)}{2} = 120,510 \text{ N/m}^2, \quad 1.2 \text{ bar} \quad (12.26)$$

Too high; the specification only allowed 0.8 overall, including the loss over the nozzles. Check the overall coefficient to see if there is room to modify the shell-side design.

$$\frac{1}{U_o} = \left( \frac{1}{683} + 0.00035 \right) \frac{19.05}{14.83} + \frac{19.05 \times 10^{-3} \ln \left( \frac{19.05}{14.88} \right)}{2 \times 55} + \frac{1}{1366} + 0.0002 \quad (12.2)$$

$$U_o = 302 \text{ W/m}^2\text{°C}$$

$$U_o \text{ required} = \frac{Q}{(A_o \Delta T_{lm})}, \quad A_o = 360 \times 0.2992 = 107.7 \text{ m}^2,$$

$$\text{so } U_o \text{ required} = \frac{1509.4 \times 10^3}{(107.7 \times 71)} = 197 \text{ W/m}^2\text{°C}$$

The estimated overall coefficient is well above that required for design, 302 compared to 192 W/m<sup>2</sup>°C, which gives scope for reducing the shell-side pressure drop.

Allow a drop of 0.1 bar for the shell inlet and outlet nozzles, leaving 0.7 bar for the shell-side flow. So, to keep within the specification, the shell-side velocity will have to be reduced by around  $\sqrt{(1/2)} = 0.707$ . To achieve this the baffle spacing will need to be increased to  $100/0.707 = 141$ , say 140 mm.

$$A_s = \frac{(23.81 - 19.05)}{23.81} 596 \times 140 = 6681 \text{ mm}^2, \quad 0.167 \text{ m}^2 \quad (12.21)$$

$$u_s = \frac{0.0076}{0.0167} = 0.455 \text{ m/s},$$

Giving:  $Re = 10,443$ ,  $h_s = 1177 \text{ W/m}^2\text{°C}$ ,  $\Delta P_s = 0.47 \text{ bar}$ , and  $U_o = 288 \text{ Wm}^{-2}\text{°C}^{-1}$ .

The pressure drop is now well within the specification.

### Step 13: Estimate cost

The cost of this design can be estimated using the methods given in Chapter 6.

### Step 14: Optimisation

There is scope for optimising the design by reducing the number of tubes, as the pressure drops are well within specification and the overall coefficient is well above that needed. However, the method used for estimating the coefficient and pressure drop on the shell-side (Kern's method) is not accurate, so keeping to this design will give some margin of safety.

**Viscosity correction factor**

The viscosity correction factor  $(\mu/\mu_w)^{0.14}$  was neglected when calculating the heat transfer coefficients and pressure drops. This is reasonable for the kerosene as it has a relatively low viscosity, but it is not so obviously so for the crude oil. So, before firming up the design, the effect of this factor on the tube-side coefficient and pressure drop will be checked.

First, an estimate of the temperature at the tube wall,  $t_w$  is needed.

$$\text{The inside area of the tubes} = \pi \times 14.83 \times 10^{-3} \times 5 \times 360 = 83.86 \text{ m}^2$$

$$\text{Heat flux} = Q/A = 1509.4 \times 10^3 / 83.86 = 17,999 \text{ W/m}^2$$

As a rough approximation

$$(t_w - t)h_i = 17,999$$

where  $t$  is the mean bulk fluid temperature = 59°C.

$$\text{So, } t_w = \frac{17,999}{680} + 59 = 86^\circ\text{C.}$$

The crude oil viscosity at this temperature =  $2.1 \times 10^{-3}$  Ns/m<sup>2</sup>.

$$\text{Giving } \left(\frac{\mu}{\mu_w}\right)^{0.14} = \left(\frac{3.2 \times 10^{-3}}{2.1 \times 10^{-3}}\right)^{0.14} = 1.06$$

Only a small factor, so the decision to neglect it was justified. Applying the correction would increase the estimated heat transfer coefficient, which is in the right direction. It would give a slight decrease in the estimated pressure drop.

**Summary: the proposed design**

Split ring, floating head, 1 shell pass, 4 tube passes.

360 carbon steel tubes, 5 m long, 19.05 mm o.d., 14.83 mm i.d., triangular pitch, pitch 23.18 mm.

Heat transfer area 107.7 m<sup>2</sup> (based on outside diameter).

Shell i.d. 597 mm (600 mm), baffle spacing 140 mm, 25% cut.

Tube-side coefficient 680 W/m<sup>2</sup>°C, clean.

Shell-side coefficient 1366 W/m<sup>2</sup>°C, clean.

Overall coefficient, estimated 288 W/m<sup>2</sup>°C, dirty.

Overall coefficient required 197 W/m<sup>2</sup>°C, dirty.

Dirt/Fouling factors:

Tube-side (crude oil) 0.00035 (W/m<sup>2</sup>°C)<sup>-1</sup>.

Shell-side (kerosene) 0.0002 (W/m<sup>2</sup>°C)<sup>-1</sup>.

Pressure drops:

Tube-side, estimated 0.40 bar, +0.1 for nozzles; specified 0.8 bar overall.

Shell-side, estimated 0.45 bar, +0.1 for nozzles; specified 0.8 bar overall.

### Optimisation using a CAD program

The use of a proprietary computer program (HTFS, M-TASC) to find the lowest cost design that meets the specification resulted in the design set out below. The program selected longer tubes, to minimise the cost. This has resulted in an exchanger with a shell length to diameter ratio of greater than 10 : 1. This could cause problems in supporting the shell, and in withdrawing the tube bundle for maintenance.

The CAD program was rerun with the tube length restricted to 3500 mm, to produce a more compact design. This gave a design with 349 tubes, 4 passes, in a shell 540 mm diameter. The setting plan for this design is shown in Figure B.

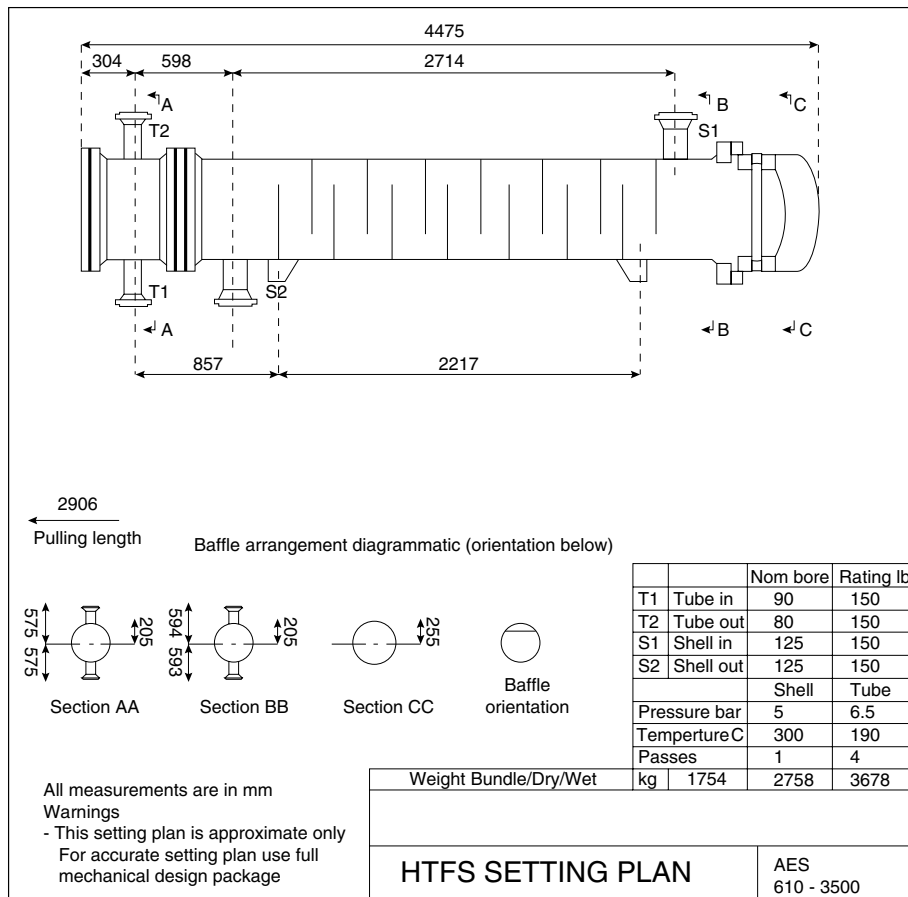


Figure B. Setting out plan for compact design. (Courtesy of Heat Transfer and Fluid Flow Service, Harwell)

### CAD design

Split ring, floating head, 1 shell pass, 2 tube passes.

168 carbon steel tubes, 6096 mm, 19.05 mm o.d., 14.83 mm i.d., triangular pitch, pitch 23.18 mm.

Heat transfer area 61 m<sup>2</sup>.  
 Shell i.d. 387, baffle spacing 77.9 mm, 15% cut.  
 Tube-side coefficient 851 W/m<sup>2</sup>°C, clean.  
 Shell-side coefficient 1191 W/m<sup>2</sup>°C, clean.  
 Overall coefficient estimated 484 Wm<sup>-2</sup>°C<sup>-1</sup> clean.  
 Overall coefficient estimated 368 Wm<sup>-2</sup>°C<sup>-1</sup> dirty.

Pressure drops, including drop over nozzles:

Tube-side, estimated 0.5 bar.  
 Shell-side, estimated 0.5 bar.

#### 12.9.4. Bell's method

In Bell's method the heat-transfer coefficient and pressure drop are estimated from correlations for flow over ideal tube-banks, and the effects of leakage, bypassing and flow in the window zone are allowed for by applying correction factors.

This approach will give more satisfactory predictions of the heat-transfer coefficient and pressure drop than Kern's method; and, as it takes into account the effects of leakage and bypassing, can be used to investigate the effects of constructional tolerances and the use of sealing strips. The procedure in a simplified and modified form to that given by Bell (1963), is outlined below.

The method is not recommended when the by-pass flow area is greater than 30% of the cross-flow area, unless sealing strips are used.

#### **Heat-transfer coefficient**

The shell-side heat transfer coefficient is given by:

$$h_s = h_{oc} F_n F_w F_b F_L \quad (12.27)$$

where  $h_{oc}$  = heat transfer coefficient calculated for cross-flow over an ideal tube bank, no leakage or bypassing.

$F_n$  = correction factor to allow for the effect of the number of vertical tube rows,

$F_w$  = window effect correction factor,

$F_b$  = bypass stream correction factor,

$F_L$  = leakage correction factor.

The total correction will vary from 0.6 for a poorly designed exchanger with large clearances to 0.9 for a well-designed exchanger.

#### **$h_{oc}$ , ideal cross-flow coefficient**

The heat-transfer coefficient for an ideal cross-flow tube bank can be calculated using the heat transfer factors  $j_h$  given in Figure 12.31. Figure 12.31 has been adapted from a similar figure given by Mueller (1973). Mueller includes values for more tube arrangements than are shown in Figure 12.31. As an alternative to Figure 12.31, the comprehensive data given

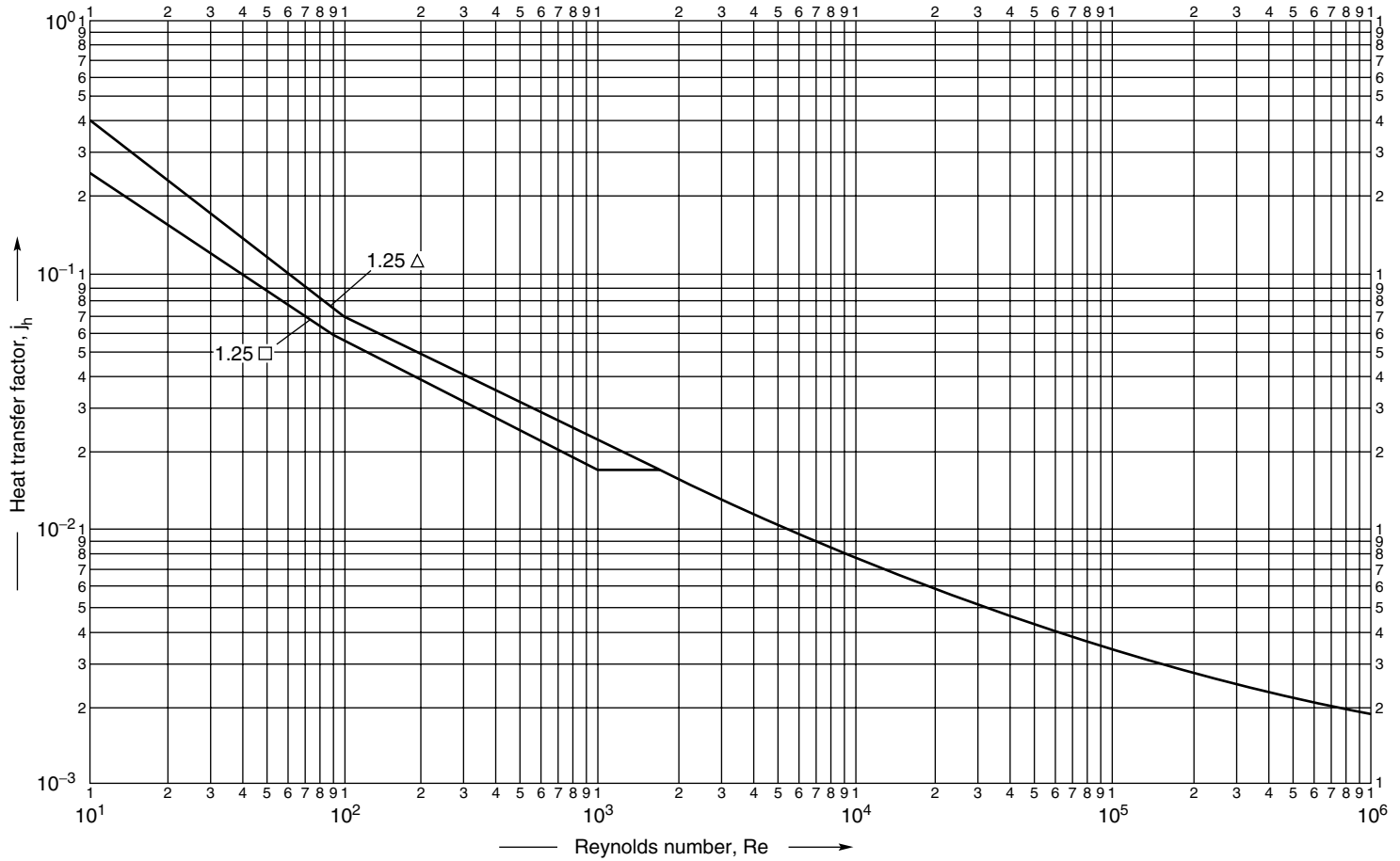


Figure 12.31. Heat-transfer factor for cross-flow tube banks

in the Engineering Sciences Data Unit Design Guide on heat transfer during cross-flow of fluids over tube banks, ESDU 73031 (1973), can be used; see Butterworth (1977).

The Reynolds number for cross-flow through a tube bank is given by:

$$Re = \frac{G_s d_o}{\mu} = \frac{u_s \rho d_o}{\mu}$$

where  $G_s$  = mass flow rate per unit area, based on the total flow and free area at the bundle equator. This is the same as  $G_s$  calculated for Kern's method,  
 $d_o$  = tube outside diameter.

The heat-transfer coefficient is given by:

$$\frac{h_{oc} d_o}{k_f} = j_h Re Pr^{1/3} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.28)$$

### **$F_n$ , tube row correction factor**

The mean heat-transfer coefficient will depend on the number of tubes crossed. Figure 12.31 is based on data for ten rows of tubes. For turbulent flow the correction factor  $F_n$  is close to 1.0. In laminar flow the heat-transfer coefficient may decrease with increasing rows of tubes crossed, due to the build up of the temperature boundary layer. The factors given below can be used for the various flow regimes; the factors for turbulent flow are based on those given by Bell (1963).

$N_{cv}$  is number of constrictions crossed = number of tube rows between the baffle tips; see Figure 12.39, and Section 12.9.5.

1.  $Re > 2000$ , turbulent;  
take  $F_n$  from Figure 12.32.

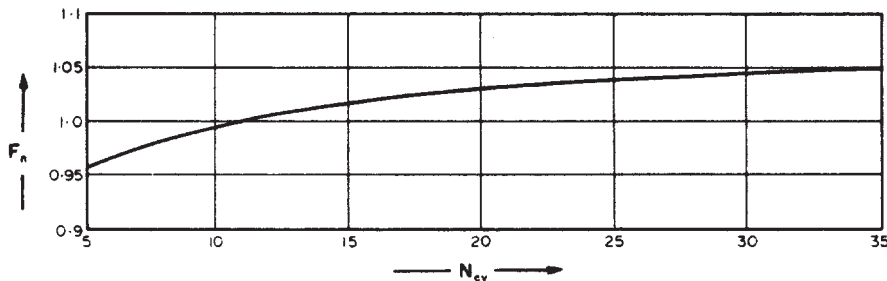


Figure 12.32. Tube row correction factor  $F_n$

2.  $Re > 100$  to 2000, transition region,  
take  $F_n = 1.0$ ;
3.  $Re < 100$ , laminar region,  

$$F_n \propto (N'_c)^{-0.18}, \quad (12.29)$$

where  $N'_c$  is the number of rows crossed in series from end to end of the shell, and depends on the number of baffles. The correction factor in the laminar region is not



well established, and Bell's paper, or the summary given by Mueller (1973), should be consulted if the design falls in this region.

### **$F_w$ , window correction factor**

This factor corrects for the effect of flow through the baffle window, and is a function of the heat-transfer area in the window zones and the total heat-transfer area. The correction factor is shown in Figure 12.33 plotted versus  $R_w$ , the ratio of the number of tubes in the window zones to the total number in the bundle, determined from the tube layout diagram.

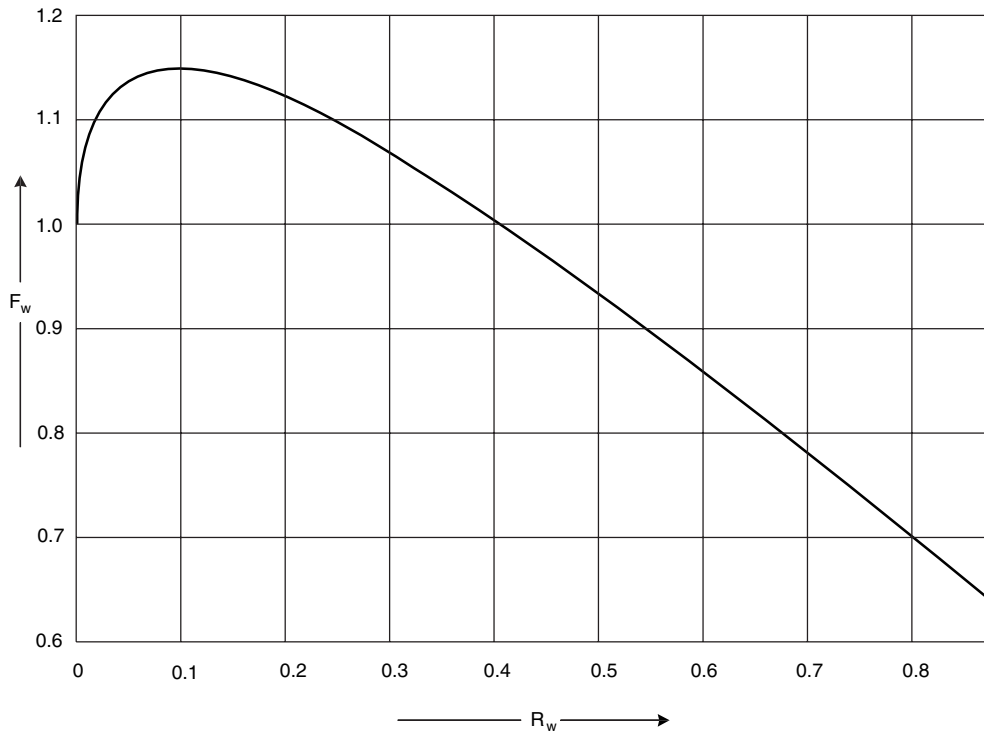


Figure 12.33. Window correction factor

For preliminary calculations  $R_w$  can be estimated from the bundle and window cross-sectional areas, see Section 12.9.5.

### **$F_b$ , bypass correction factor**

This factor corrects for the main bypass stream, the flow between the tube bundle and the shell wall, and is a function of the shell to bundle clearance, and whether sealing strips are used:

$$F_b = \exp \left[ -\alpha \frac{A_b}{A_s} \left( 1 - \left( \frac{2N_s}{N_{cv}} \right)^{1/3} \right) \right] \quad (12.30)$$

where  $\alpha = 1.5$  for laminar flow,  $Re < 100$ ,

$\alpha = 1.35$  for transitional and turbulent flow  $Re > 100$ ,

$A_b$  = clearance area between the bundle and the shell, see Figure 12.39 and Section 12.9.5,

$A_s$  = maximum area for cross-flow, equation 12.21,

$N_s$  = number of sealing strips encountered by the bypass stream in the cross-flow zone,

$N_{cv}$  = the number of constrictions, tube rows, encountered in the cross-flow section.

Equation 12.30 applies for  $N_s \leq N_{cv}/2$ .

Where no sealing strips are used,  $F_b$  can be obtained from Figure 12.34.

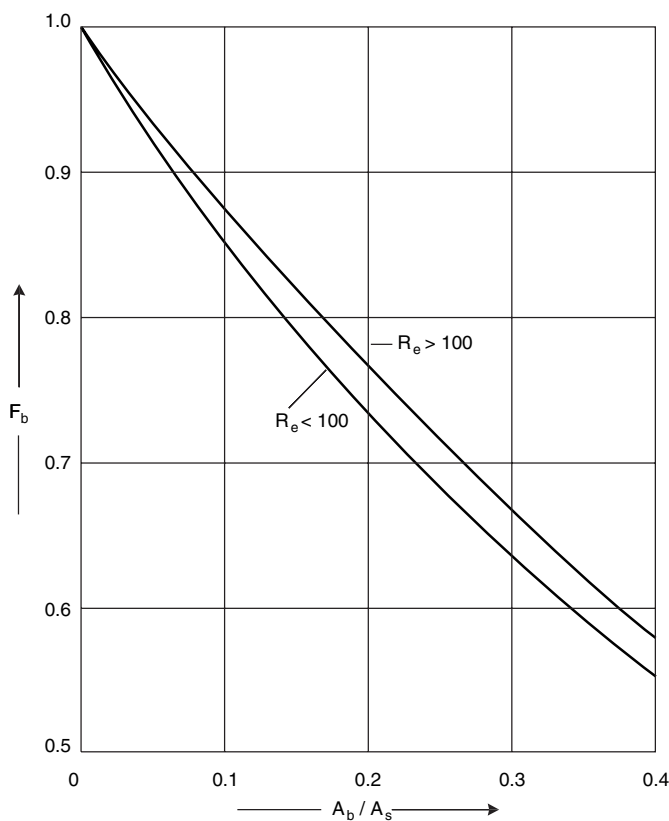


Figure 12.34. Bypass correction factor

### **$F_L$ , Leakage correction factor**

This factor corrects for the leakage through the tube-to-baffle clearance and the baffle-to-shell clearance.

$$F_L = 1 - \beta_L \left[ \frac{(A_{tb} + 2A_{sb})}{A_L} \right] \quad (12.31)$$

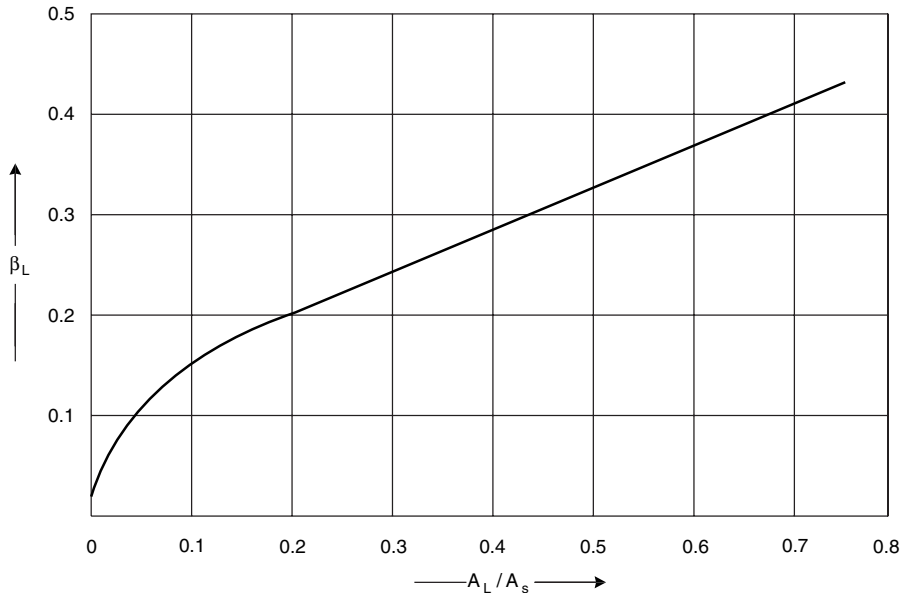


Figure 12.35. Coefficient for  $F_L$ , heat transfer

where  $\beta_L$  = a factor obtained from Figure 12.35,

$A_{tb}$  = the tube to baffle clearance area, per baffle, see Figure 12.39 and Section 12.9.5,

$A_{sb}$  = shell-to-baffle clearance area, per baffle, see Figure 12.39 and Section 12.9.5,

$A_L$  = total leakage area =  $(A_{tb} + A_{sb})$ .

Typical values for the clearances are given in the standards, and are discussed in Section 12.5.6. The clearances and tolerances required in practical exchangers are discussed by Rubin (1968).

### **Pressure drop**

The pressure drops in the cross-flow and window zones are determined separately, and summed to give the total shell-side pressure drop.

### **Cross-flow zones**

The pressure drop in the cross-flow zones between the baffle tips is calculated from correlations for ideal tube banks, and corrected for leakage and bypassing.

$$\Delta P_c = \Delta P_i F'_b F'_L \quad (12.32)$$

where  $\Delta P_c$  = the pressure drop in a cross-flow zone between the baffle tips, corrected for by-passing and leakage,

$\Delta P_i$  = the pressure drop calculated for an equivalent ideal tube bank,

$F'_b$  = by-pass correction factor,

$F'_L$  = leakage correction factor.

### **$\Delta P_i$ ideal tube bank pressure drop**

The number of tube rows has little effect on the friction factor and is ignored.

Any suitable correlation for the cross-flow friction factor can be used; for that given in Figure 12.36, the pressure drop across the ideal tube bank is given by:

$$\Delta P_i = 8j_f N_{cv} \frac{\rho u_s^2}{2} \left( \frac{\mu}{\mu_w} \right)^{-0.14} \quad (12.33)$$

where  $N_{cv}$  = number of tube rows crossed (in the cross-flow region),

$u_s$  = shell side velocity, based on the clearance area at the bundle equator, equation 12.21,

$j_f$  = friction factor obtained from Figure 12.36, at the appropriate Reynolds number,  $Re = (\rho u_s d_o / \mu)$ .

### **$F'_b$ , bypass correction factor for pressure drop**

Bypassing will affect the pressure drop only in the cross-flow zones. The correction factor is calculated from the equation used to calculate the bypass correction factor for heat transfer, equation 12.30, but with the following values for the constant  $\alpha$ .

Laminar region,  $Re < 100$ ,  $\alpha = 5.0$

Transition and turbulent region,  $Re > 100$ ,  $\alpha = 4.0$

The correction factor for exchangers without sealing strips is shown in Figure 12.37.

### **$F'_L$ , leakage factor for pressure drop**

Leakages will affect the pressure drop in both the cross-flow and window zones. The factor is calculated using the equation for the heat-transfer leakage-correction factor, equation 12.31, with the values for the coefficient  $\beta'_L$  taken from Figure 12.38.

### **Window-zone pressure drop**

Any suitable method can be used to determine the pressure drop in the window area; see Butterworth (1977). Bell used a method proposed by Colburn. Corrected for leakage, the window drop for turbulent flow is given by:

$$\Delta P_w = F'_L (2 + 0.6N_{wv}) \frac{\rho u_z^2}{2} \quad (12.34)$$

where  $u_z$  = the geometric mean velocity,

$$u_z = \sqrt{u_w u_s},$$

$u_w$  = the velocity in the window zone, based on the window area less the area occupied by the tubes  $A_w$ , see Section 12.9.5,

$$u_w = \frac{W_s}{A_w \rho} \quad (12.35)$$

$W_s$  = shell-side fluid mass flow, kg/s,

$N_{wv}$  = number of restrictions for cross-flow in window zone, approximately equal to the number of tube rows.

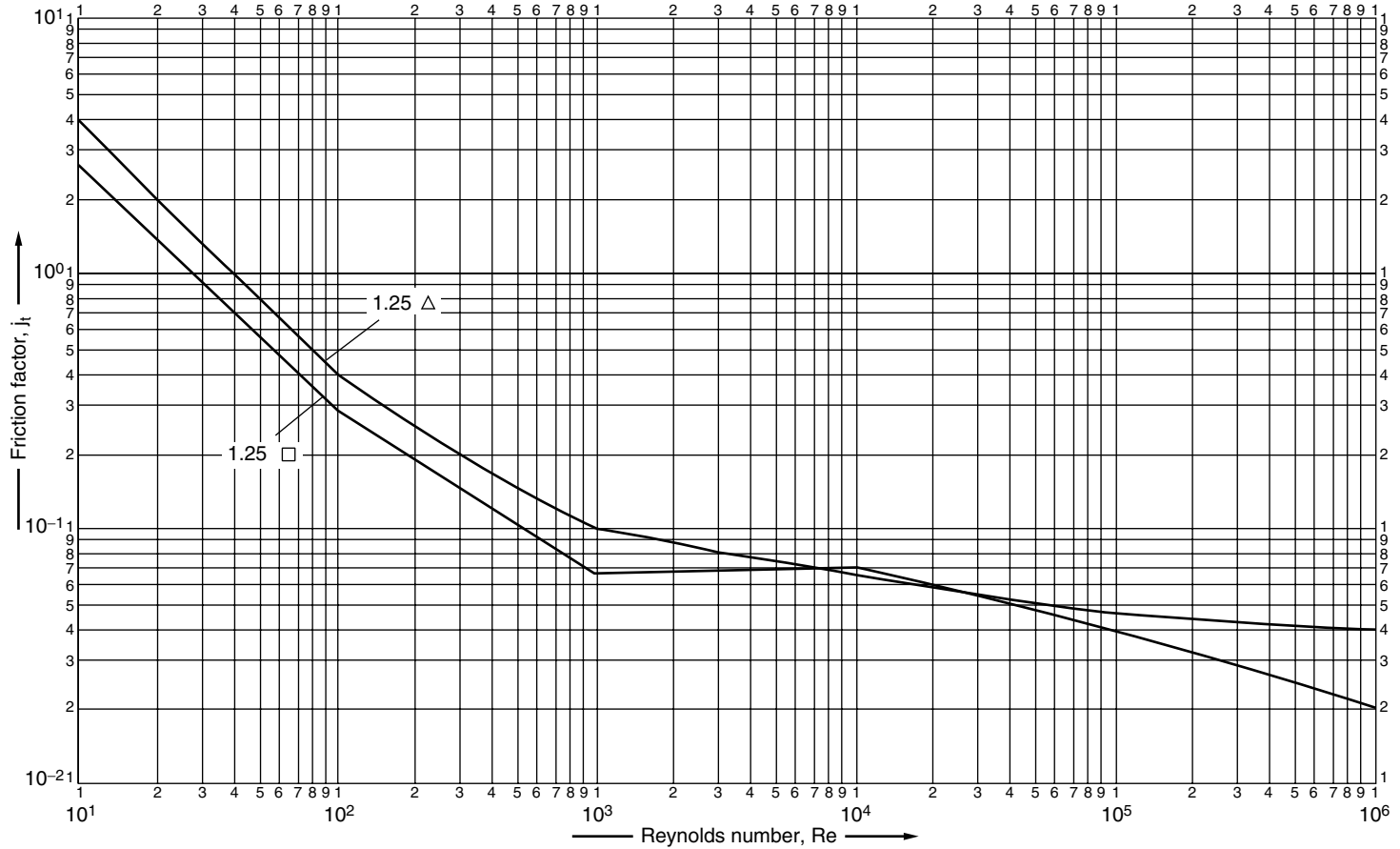
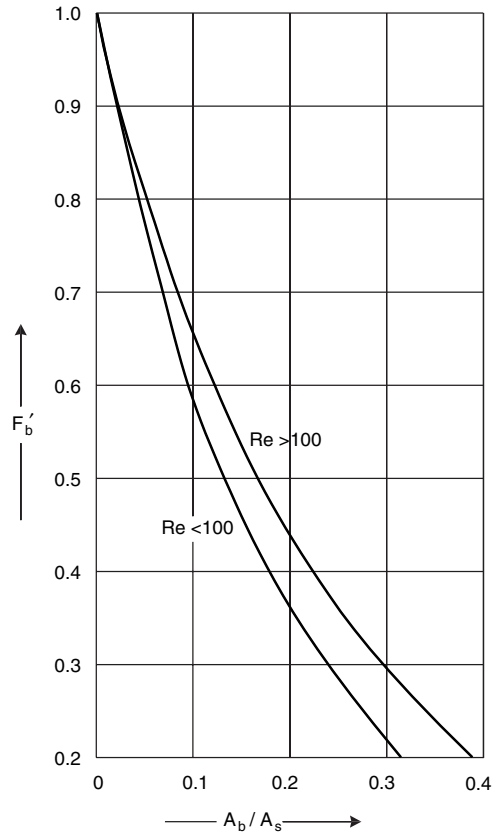
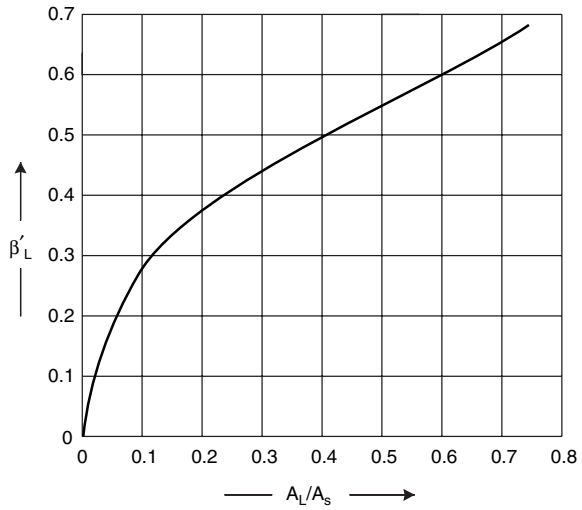


Figure 12.36. Friction factor for cross-flow tube banks

Figure 12.37. Bypass factor for pressure drop  $F'_b$ Figure 12.38. Coefficient for  $F'_L$ , pressure drop

### **End zone pressure drop**

There will be no leakage paths in an end zone (the zone between tube sheet and baffle). Also, there will only be one baffle window in these zones; so the total number of restrictions in the cross-flow zone will be  $N_{cv} + N_{wv}$ . The end zone pressure drop  $\Delta P_e$  will therefore be given by:

$$\Delta P_e = \Delta P_i \left[ \frac{(N_{wv} + N_{cv})}{N_{cv}} \right] F'_b \quad (12.36)$$

### **Total shell-side pressure drop**

Summing the pressure drops over all the zones in series from inlet to outlet gives:

$$\begin{aligned} \Delta P_s &= 2 \text{ end zones} + (N_b - 1) \text{ cross-flow zones} + N_b \text{ window zones} \\ \Delta P_s &= 2\Delta P_e + \Delta P_c(N_b - 1) + N_b\Delta P_w \end{aligned} \quad (12.37)$$

where  $N_b$  is the number of baffles =  $[(L/l_B) - 1]$ .

An estimate of the pressure loss incurred in the shell inlet and outlet nozzles must be added to that calculated by equation 12.37; see Section 12.9.3.

### **End zone lengths**

The spacing in the end zones will often be increased to provide more flow area at the inlet and outlet nozzles. The velocity in these zones will then be lower and the heat transfer and pressure drop will be reduced slightly. The effect on pressure drop will be more marked than on heat transfer, and can be estimated by using the actual spacing in the end zone when calculating the cross-flow velocity in those zones.

## **12.9.5. Shell and bundle geometry**

The bypass and leakage areas, window area, and the number of tubes and tube rows in the window and cross-flow zones can be determined precisely from the tube layout diagram. For preliminary calculations they can be estimated with sufficient accuracy by considering the tube bundle and shell geometry.

With reference to Figures 12.39 and 12.40:

$H_c$  = baffle cut height =  $D_s \times B_c$ , where  $B_c$  is the baffle cut as a fraction,

$H_b$  = height from the baffle chord to the top of the tube bundle,

$B_b$  = "bundle cut" =  $H_b/D_b$ ,

$\theta_b$  = angle subtended by the baffle chord, rads,

$D_b$  = bundle diameter.

Then:

$$H_b = \frac{D_b}{2} - D_s(0.5 - B_c) \quad (12.38)$$

$$N_{cv} = \frac{(D_b - 2H_b)}{p'_i} \quad (12.39)$$

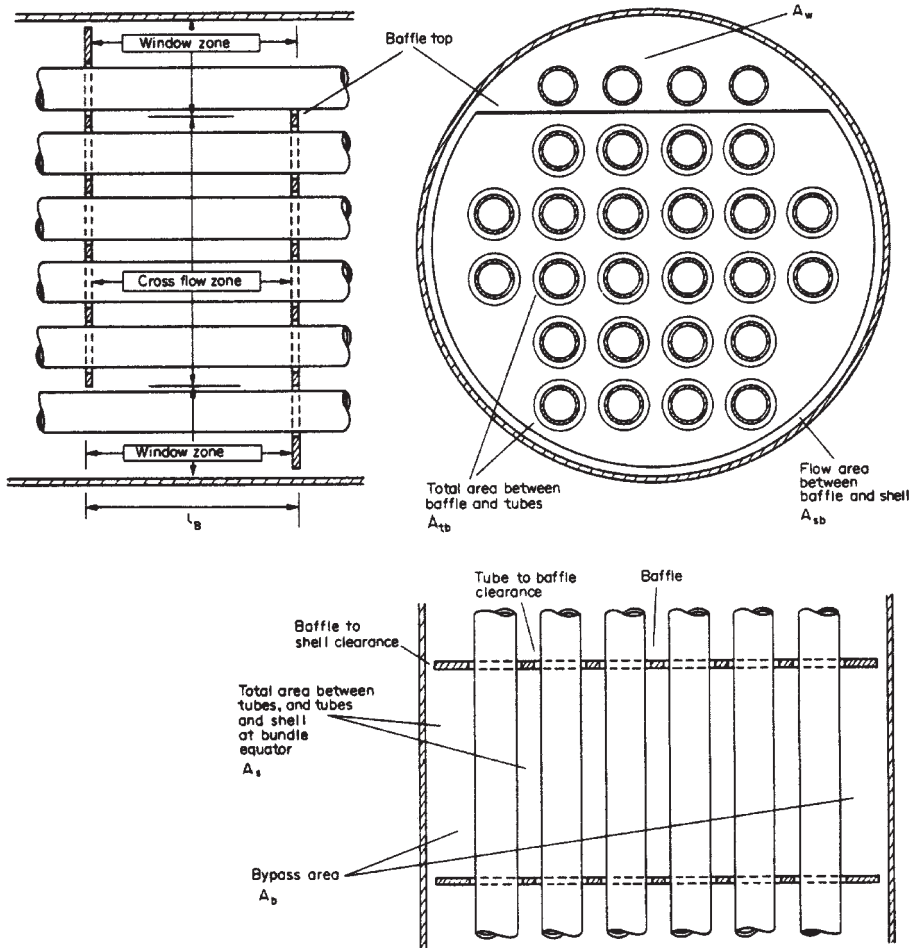


Figure 12.39. Clearance and flow areas in the shell-side of a shell and tube exchanger

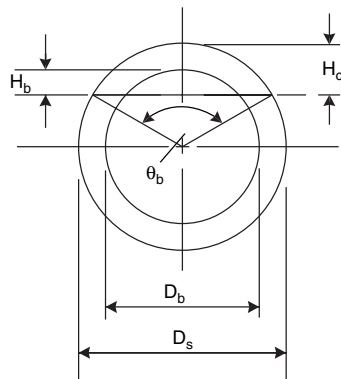


Figure 12.40. Baffle and tube geometry



$$N_{wv} = \frac{H_b}{p'_t} \quad (12.40)$$

where  $p'_t$  is the vertical tube pitch

$$p'_t = p_t \text{ for square pitch,}$$

$$p'_t = 0.87 p_t \text{ for equilateral triangular pitch.}$$

The number of tubes in a window zone  $N_w$  is given by:

$$N_w = N_t \times R'_a \quad (12.41)$$

where  $R'_a$  is the ratio of the bundle cross-sectional area in the window zone to the total bundle cross-sectional area,  $R'_a$  can be obtained from Figure 12.41, for the appropriate "bundle cut",  $B_b$ .

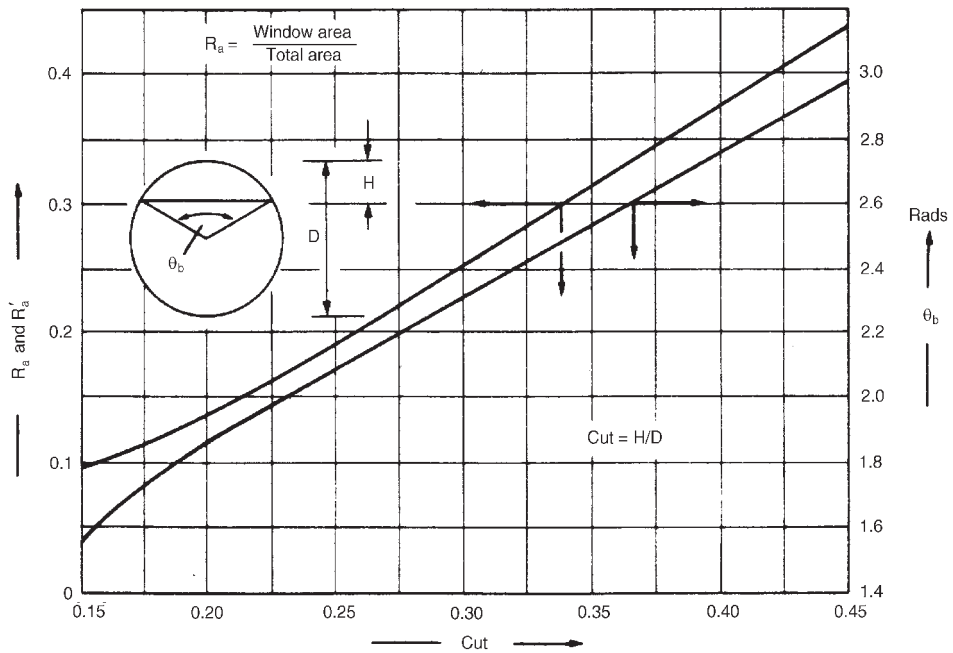


Figure 12.41. Baffle geometrical factors

The number of tubes in a cross-flow zone  $N_c$  is given by

$$N_c = N_t - 2N_w \quad (12.42)$$

and

$$R_w = \frac{2N_w}{N_t} \quad (12.43)$$

$$A_w = \left( \frac{\pi D_s^2}{4} \times R_a \right) - \left( N_w \frac{\pi d_o^2}{4} \right) \quad (12.44)$$

$R_a$  is obtained from Figure 12.41, for the appropriate baffle cut  $B_c$

$$A_{tb} = \frac{c_t \pi d_o}{2} (N_t - N_w) \quad (12.45)$$

where  $c_t$  is the diametrical tube-to-baffle clearance; the difference between the hole and tube diameter, typically 0.8 mm.

$$A_{sb} = \frac{c_s D_s}{2} (2\pi - \theta_b) \quad (12.46)$$

where  $c_s$  is the baffle-to-shell clearance, see Table 12.5.

$\theta_b$  can be obtained from Figure 12.41, for the appropriate baffle cut,  $B_c$

$$A_b = l_B (D_s - D_b) \quad (12.47)$$

where  $l_B$  is the baffle spacing.

### 12.9.6. Effect of fouling on pressure drop

Bell's method gives an estimate of the shell-side pressure drop for the exchanger in the clean condition. In service, the clearances will tend to plug up, particularly the small clearance between the tubes and baffle, and this will increase the pressure drop. Devore (1961) has estimated the effect of fouling on pressure drop by calculating the pressure drop in an exchange in the clean condition and with the clearance reduced by fouling, using Tinker's method. He presented his results as ratios of the fouled to clean pressure drop for various fouling factors and baffle spacings.

The ratios given in Table 12.7, which are adapted from Devore's figures, can be used to make a rough estimate of the effect of fouling on pressure drop.

Table 12.7. Ratio of fouled to clean pressure drop

Fouling coefficient (W/m <sup>2</sup> °C)	Shell diameter/baffle spacing		
	1.0	2.0	5.0
<i>Laminar flow</i>			
6000	1.06	1.20	1.28
2000	1.19	1.44	1.55
<1000	1.32	1.99	2.38
<i>Turbulent flow</i>			
6000	1.12	1.38	1.55
2000	1.37	2.31	2.96
<1000	1.64	3.44	4.77

### 12.9.7. Pressure-drop limitations

Though Bell's method will give a better estimate of the shell-side pressure drop than Kern's, it is not sufficiently accurate for the design of exchangers where the allowable pressure drop is the overriding consideration. For such designs, a divided-flow model based on Tinker's work should be used. If a proprietary computer program is not available,

the ESDU Design Guide, ESDU 83038 (1984) is recommended. Devore's method can also be considered, providing the exchanger layout conforms with those covered in his work.

### Example 12.4

Using Bell's method, calculate the shell-side heat transfer coefficient and pressure drop for the exchanger designed in Example 12.1.

Summary of proposed design

Number of tubes	= 918
Shell i.d.	894 mm
Bundle diameter	826 mm
Tube o.d.	20 mm
Pitch 1.25 $\Delta$	25 mm
Tube length	4830 mm
Baffle pitch	356 mm

Physical properties from Example 12.1

### Solution

#### **Heat-transfer coefficient**

Ideal bank coefficient,  $h_{oc}$

$$A_s = \frac{25 - 20}{25} \times 894 \times 356 \times 10^{-6} = 0.062 \text{ m}^2 \quad (12.21)$$

$$G_s = \frac{100,000}{3600} \times \frac{1}{0.062} = 448 \text{ kg/s m}^2$$

$$Re = \frac{G_s d_o}{\mu} = \frac{448 \times 20 \times 10^{-3}}{0.34 \times 10^{-3}} = 26,353$$

From Figure 12.31  $j_h = 5.3 \times 10^{-3}$ .

Prandtl number, from Example 12.1 = 5.1

Neglect viscosity correction factor ( $\mu/\mu_w$ ).

$$h_{oc} = \frac{0.19}{20 \times 10^{-3}} \times 5.3 \times 10^{-3} \times 26,353 \times 5.1^{1/3} = 2272 \text{ W/m}^2\text{°C} \quad (12.28)$$

#### **Tube row correction factor, $F_n$**

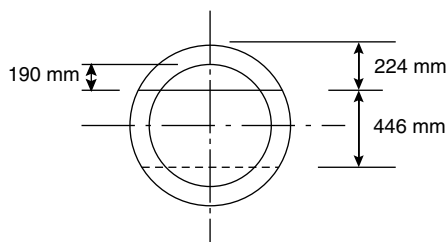
Tube vertical pitch  $p'_t = 0.87 \times 25 = 21.8 \text{ mm}$

Baffle cut height  $H_c = 0.25 \times 894 = 224 \text{ mm}$

Height between baffle tips =  $894 - 2 \times 224 = 446 \text{ mm}$

$$N_{cv} = \frac{446}{21.8} = 20$$

From Figure 12.32  $F_n = 1.03$ .

**Window correction factor,  $F_w$** 

$$H_b = \frac{826}{2} - 894(0.5 - 0.25) = 190 \text{ mm} \quad (12.38)$$

“Bundle cut” =  $190/826 = 0.23$  (23 per cent)

From Figure 12.41 at cut of 0.23

$$R'_a = 0.18$$

$$\text{Tubes in one window area, } N_w = 918 \times 0.18 = 165 \quad (12.41)$$

$$\text{Tubes in cross-flow area, } N_c = 918 - 2 \times 165 = 588 \quad (12.42)$$

$$R_w = \frac{2 \times 165}{918} = 0.36 \quad (12.43)$$

From Figure 12.33  $F_w = 1.02$ .

**Bypass correction,  $F_b$** 

$$A_b = (894 - 826)356 \times 10^{-6} = 0.024 \text{ m}^2 \quad (12.47)$$

$$\frac{A_b}{A_s} = \frac{0.024}{0.062} = 0.39$$

$$F_b = \exp[-1.35 \times 0.39] = 0.59 \quad (12.30)$$

Very low, sealing strips needed; try one strip for each five vertical rows.

$$\frac{N_s}{N_{cv}} = \frac{1}{5}$$

$$F_b = \exp[-1.35 \times 0.39(1 - (\frac{2}{5})^{1/3})] = 0.87 \quad (12.30)$$

**Leakage correction,  $F_L$** 

Using clearances as specified in the Standards,

$$\text{tube-to-baffle } \frac{1}{32} \text{ in.} = 0.8 \text{ mm}$$

$$\text{baffle-to-shell } \frac{3}{16} \text{ in.} = 4.8 \text{ mm}$$

$$A_{lb} = \frac{0.8}{2} \times 20\pi(918 - 165) = 18.9 \times 10^3 \text{ mm}^2 = 0.019 \text{ m}^2 \quad (12.45)$$

From Figure 12.41, 25 per cent cut (0.25),  $\theta_b = 2.1$  rads.

$$A_{sb} = \frac{4.8}{2} \times 894(2\pi - 2.1) = 8.98 \times 10^3 \text{ mm}^2 = 0.009 \text{ m}^2 \quad (12.46)$$

$$A_L = (0.019 + 0.009) = 0.028 \text{ m}^2$$

$$\frac{A_L}{A_s} = \frac{0.028}{0.062} = 0.45$$

From Figure 12.35  $\beta_L = 0.3$ .

$$F_L = 1 - 0.3 \left[ \frac{(0.019 + 2 \times 0.009)}{0.028} \right] = 0.60 \quad (12.31)$$

### **Shell-side coefficient**

$$h_s = 2272 \times 1.03 \times 1.02 \times 0.87 \times 0.60 = \underline{\underline{1246 \text{ W/m}^2\text{°C}}} \quad (12.27)$$

Appreciably lower than that predicted by Kern's method.

### **Pressure drop**

#### **Cross-flow zone**

From Figure 12.36 at  $Re = 26,353$ , for 1.25  $\Delta$  pitch,  $j_f = 5.6 \times 10^{-2}$

$$u_s = \frac{G_s}{\rho} = \frac{448}{750} = 0.60 \text{ m/s}$$

Neglecting viscosity term ( $\mu/\mu_w$ ).

$$\Delta P_i = 8 \times 5.6 \times 10^{-2} \times 20 \times \frac{750 \times 0.6^2}{2} = 1209.6 \text{ N/m}^2 \quad (12.33)$$

$$(\alpha = 4.0) \quad (12.30)$$

$$F'_b = \exp[-4.0 \times 0.39(1 - (\frac{2}{5})^{1/3})] = 0.66$$

From Figure 12.38  $\beta'_L = 0.52$ .

$$F'_L = 1 - 0.52 \left[ \frac{(0.019 + 2 \times 0.009)}{0.028} \right] = 0.31 \quad (12.31)$$

$$\Delta P_c = 1209.6 \times 0.66 \times 0.31 = 248 \text{ N/m}^2$$

#### **Window zone**

From Figure 12.41, for baffle cut 25 per cent (0.25)  $R_a = 0.19$ .

$$\begin{aligned} A_w &= \left( \frac{\pi}{4} \times 894^2 \times 0.19 \right) - \left( 165 \times \frac{\pi}{4} \times 20^2 \right) \\ &= 67.4 \times 10^3 \text{ mm}^2 = 0.067 \text{ m}^2 \end{aligned} \quad (12.44)$$

$$u_w = \frac{100,000}{3600} \times \frac{1}{750} \times \frac{1}{0.067} = 0.55 \text{ m/s}$$

$$u_z = \sqrt{u_w u_s} = \sqrt{0.55 \times 0.60} = 0.57 \text{ m/s}$$

$$N_{wv} = \frac{190}{21.8} = 8 \quad (12.40)$$

$$\Delta P_w = 0.31(2 + 0.6 \times 8) \frac{750 \times 0.57^2}{2} = 257 \text{ N/m}^2 \quad (12.34)$$

*End zone*

$$\Delta P_e = 1209.6 \left[ \frac{(8 + 20)}{20} \right] 0.66 = 1118 \text{ N/m}^2 \quad (12.36)$$

*Total pressure drop*

$$\text{Number of baffles } N_b = \frac{4830}{356} - 1 = 12$$

$$\Delta P_s = 2 \times 1118 + 248(12 - 1) + 12 \times 257 = 8048 \text{ N/m}^2 \quad (12.37)$$

$$= \underline{\underline{8.05 \text{ kPa}}} \quad (1.2 \text{ psi})$$

This for the exchanger in the clean condition. Using the factors given in Table 12.7 to estimate the pressure drop in the fouled condition

$$\Delta P_s = 1.4 \times 8.05 = \underline{\underline{11.3 \text{ kPa}}}$$

Appreciably lower than that predicted by Kern's method. This shows the unsatisfactory nature of the methods available for predicting the shell-side pressure drop.

## 12.10. CONDENSERS

This section covers the design of shell and tube exchangers used as condensers. Direct contact condensers are discussed in Section 12.13.

The construction of a condenser will be similar to other shell and tube exchangers, but with a wider baffle spacing, typically  $l_B = D_s$ .

Four condenser configurations are possible:

1. Horizontal, with condensation in the shell, and the cooling medium in the tubes.
2. Horizontal, with condensation in the tubes.
3. Vertical, with condensation in the shell.
4. Vertical, with condensation in the tubes.

Horizontal shell-side and vertical tube-side are the most commonly used types of condenser. A horizontal exchanger with condensation in the tubes is rarely used as a process condenser, but is the usual arrangement for heaters and vaporisers using condensing steam as the heating medium.

### 12.10.1. Heat-transfer fundamentals

The fundamentals of condensation heat transfer are covered in Volume 1, Chapter 9.

The normal mechanism for heat transfer in commercial condensers is filmwise condensation. Dropwise condensation will give higher heat-transfer coefficients, but is unpredictable; and is not yet considered a practical proposition for the design of condensers for general purposes.

The basic equations for filmwise condensation were derived by Nusselt (1916), and his equations form the basis for practical condenser design. The basic Nusselt equations are derived in Volume 1, Chapter 9. In the Nusselt model of condensation laminar flow is assumed in the film, and heat transfer is assumed to take place entirely by conduction through the film. In practical condensers the Nusselt model will strictly only apply at low liquid and vapour rates, and where the flowing condensate film is undisturbed. Turbulence can be induced in the liquid film at high liquid rates, and by shear at high vapour rates. This will generally increase the rate of heat transfer over that predicted using the Nusselt model. The effect of vapour shear and film turbulence are discussed in Volume 1, Chapter 9, see also Butterworth (1978) and Taborek (1974).

Developments in the theory of condensation and their application in condenser design are reviewed by Owen and Lee (1983).

#### **Physical properties**

The physical properties of the condensate for use in the following equations, are evaluated at the average condensate film temperature: the mean of the condensing temperature and the tube-wall temperature.

### 12.10.2. Condensation outside horizontal tubes

$$(h_c)_1 = 0.95k_L \left[ \frac{\rho_L(\rho_L - \rho_v)g}{\mu_L\Gamma} \right]^{1/3} \quad (12.48)$$

where  $(h_c)_1$  = mean condensation film coefficient, for a single tube,  $\text{W/m}^2\text{°C}$

$k_L$  = condensate thermal conductivity,  $\text{W/m}^{\circ}\text{C}$ ,

$\rho_L$  = condensate density,  $\text{kg/m}^3$ ,

$\rho_v$  = vapour density,  $\text{kg/m}^3$ ,

$\mu_L$  = condensate viscosity,  $\text{Ns/m}^2$ ,

$g$  = gravitational acceleration,  $9.81 \text{ m/s}^2$ ,

$\Gamma$  = the tube loading, the condensate flow per unit length of tube,  $\text{kg/m s}$ .

In a bank of tubes the condensate from the upper rows of tubes will add to that condensing on the lower tubes. If there are  $N_r$  tubes in a vertical row and the condensate is assumed to flow smoothly from row to row, Figure 12.42a, and if the flow remains laminar, the mean coefficient predicted by the Nusselt model is related to that for the top tube by:

$$(h_c)_{N_r} = (h_c)_1 N_r^{-1/4} \quad (12.49)$$

In practice, the condensate will not flow smoothly from tube to tube, Figure 12.42b, and the factor of  $(N_r)^{-1/4}$  applied to the single tube coefficient in equation 12.49 is considered to be too conservative. Based on results from commercial exchangers, Kern (1950)

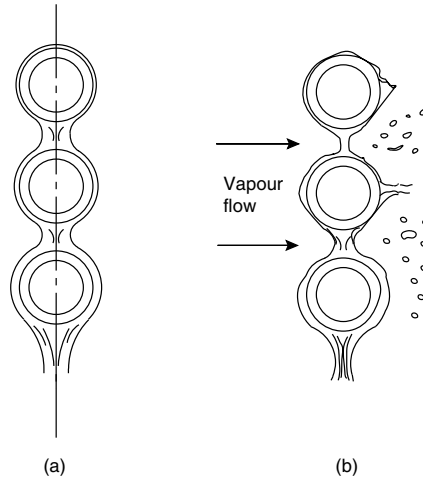


Figure 12.42. Condensate flow over tube banks

suggests using an index of  $1/6$ . Frank (1978) suggests multiplying single tube coefficient by a factor of 0.75.

Using Kern's method, the mean coefficient for a tube bundle is given by:

$$(h_c)_b = 0.95k_L \left[ \frac{\rho_L(\rho_L - \rho_v)g}{\mu_L \Gamma_h} \right]^{1/3} N_r^{-1/6} \quad (12.50)$$

where  $\Gamma_h = \frac{W_c}{LN_t}$

and  $L =$  tube length,

$W_c =$  total condensate flow,

$N_t =$  total number of tubes in the bundle,

$N_r =$  average number of tubes in a vertical tube row.

$N_r$  can be taken as two-thirds of the number in the central tube row.

For low-viscosity condensates the correction for the number of tube rows is generally ignored.

A procedure for estimating the shell-side heat transfer in horizontal condensers is given in the Engineering Sciences Data Unit Design Guide, ESDU 84023.

### 12.10.3. Condensation inside and outside vertical tubes

For condensation inside and outside vertical tubes the Nusselt model gives:

$$(h_c)_v = 0.926k_L \left[ \frac{\rho_L(\rho_L - \rho_v)g}{\mu_L \Gamma_v} \right]^{1/3} \quad (12.51)$$

where  $(h_c)_v =$  mean condensation coefficient,  $W/m^2 \cdot ^\circ C$ ,

$\Gamma_v =$  vertical tube loading, condensate rate per unit tube perimeter,  $kg/m \cdot s$



for a tube bundle

$$\Gamma_v = \frac{W_c}{N_t \pi d_o} \text{ or } \frac{W_c}{N_t \pi d_i}$$

Equation 12.51 will apply up to a Reynolds number of 30; above this value waves on the condensate film become important. The Reynolds number for the condensate film is given by:

$$Re_c = \frac{4\Gamma_v}{\mu_L}$$

The presence of waves will increase the heat-transfer coefficient, so the use of equation 12.51 above a Reynolds number of 30 will give conservative (safe) estimates. The effect of waves on condensate film on heat transfer is discussed by Kutateladze (1963).

Above a Reynolds number of around 2000, the condensate film becomes turbulent. The effect of turbulence in the condensate film was investigated by Colburn (1934) and Colburn's results are generally used for condenser design, Figure 12.43. Equation 12.51 is also shown on Figure 12.43. The Prandtl number for the condensate film is given by:

$$Pr_c = \frac{C_p \mu_L}{k_L}$$

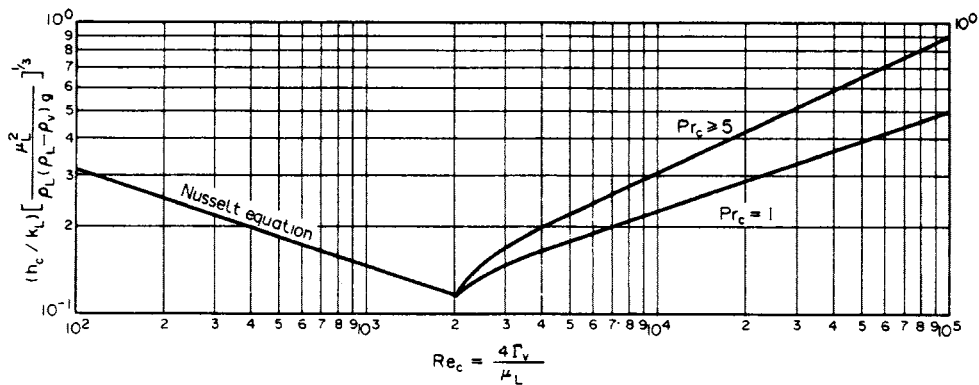


Figure 12.43. Condensation coefficient for vertical tubes

Figure 12.43 can be used to estimate condensate film coefficients in the absence of appreciable vapour shear. Horizontal and downward vertical vapour flow will increase the rate of heat transfer, and the use of Figure 12.43 will give conservative values for most practical condenser designs.

Boyko and Kruzhilin (1967) developed a correlation for shear-controlled condensation in tubes which is simple to use. Their correlation gives the mean coefficient between two points at which the vapour quality is known. The vapour quality  $x$  is the mass fraction of

the vapour present. It is convenient to represent the Boyko-Kruzhilin correlation as:

$$(h_c)_{BK} = h'_i \left[ \frac{J_1^{1/2} + J_2^{1/2}}{2} \right] \quad (12.52)$$

where

$$J = 1 + \left[ \frac{\rho_L - \rho_v}{\rho_v} \right] x$$

and the suffixes 1 and 2 refer to the inlet and outlet conditions respectively.  $h'_i$  is the tube-side coefficient evaluated for single-phase flow of the total condensate (the condensate at point 2). That is, the coefficient that would be obtained if the condensate filled the tube and was flowing alone; this can be evaluated using any suitable correlation for forced convection in tubes; see Section 12.8.

Boyko and Kruzhilin used the correlation:

$$h'_i = 0.021 \left( \frac{k_L}{d_i} \right) Re^{0.8} Pr^{0.43} \quad (12.53)$$

In a condenser the inlet stream will normally be saturated vapour and the vapour will be totally condensed.

For these conditions equation 12.52 becomes:

$$(h_c)_{BK} = h'_i \left[ \frac{1 + \sqrt{\rho_L/\rho_v}}{2} \right] \quad (12.54)$$

For the design of condensers with condensation inside the tubes and downward vapour flow, the coefficient should be evaluated using Figure 12.43 and equation 12.52, and the *higher* value selected.

### **Flooding in vertical tubes**

When the vapour flows up the tube, which will be the usual arrangement for a reflux condenser, care must be taken to ensure that the tubes do not flood. Several correlations have been published for the prediction of flooding in vertical tubes, see Perry *et al.* (1997). One of the simplest to apply, which is suitable for use in the design of condensers handling low-viscosity condensates, is the criterion given by Hewitt and Hall-Taylor (1970); see also Butterworth (1977). Flooding should not occur if the following condition is satisfied:

$$[u_v^{1/2} \rho_v^{1/4} + u_L^{1/2} \rho_L^{1/4}] < 0.6 [gd_i(\rho_L - \rho_v)]^{1/4} \quad (12.55)$$

where  $u_v$  and  $u_L$  are the velocities of the vapour and liquid, based on each phase flowing in the tube alone; and  $d_i$  is in metres. The critical condition will occur at the bottom of the tube, so the vapour and liquid velocities should be evaluated at this point.

### **Example 12.5**

Estimate the heat-transfer coefficient for steam condensing on the outside, and on the inside, of a 25 mm o.d., 21 mm i.d. vertical tube 3.66 m long. The steam condensate rate

is 0.015 kg/s per tube and condensation takes place at 3 bar. The steam will flow down the tube.

### Solution

Physical properties, from steam tables:

$$\text{Saturation temperature} = 133.5^\circ\text{C}$$

$$\rho_L = 931 \text{ kg/m}^3$$

$$\rho_v = 1.65 \text{ kg/m}^3$$

$$k_L = 0.688 \text{ W/m}^\circ\text{C}$$

$$\mu_L = 0.21 \text{ mNs/m}^2$$

$$Pr_c = 1.27$$

### Condensation outside the tube

$$\Gamma_v = \frac{0.015}{\pi 25 \times 10^{-3}} = 0.191 \text{ kg/s m}$$

$$Re_c = \frac{4 \times 0.191}{0.21 \times 10^{-3}} = 3638$$

From Figure 12.43

$$\frac{h_c}{k_L} \left[ \frac{\mu_L^2}{\rho_L(\rho_L - \rho_v)g} \right]^{1/3} = 1.65 \times 10^{-1}$$

$$h_c = 1.65 \times 10^{-1} \times 0.688 \left[ \frac{(0.21 \times 10^{-3})^2}{931(931 - 1.65)9.81} \right]^{-1/3}$$

$$= \underline{\underline{6554 \text{ W/m}^2\text{C}}}$$

### Condensation inside the tube

$$\Gamma_v = \frac{0.015}{\pi 21 \times 10^{-3}} = 0.227 \text{ kg/s m}$$

$$Re_c = \frac{4 \times 0.227}{0.21 \times 10^{-3}} = 4324$$

From Figure 12.43

$$h_c = 1.72 \times 10^{-1} \times 0.688 \left[ \frac{(0.21 \times 10^{-3})^2}{931(931 - 1.65)9.81} \right]^{-1/3}$$

$$= 6832 \text{ W/m}^2\text{C}$$

Boyko-Kruzhilin method

$$\text{Cross-sectional area of tube} = (21 \times 10^{-3})^2 \frac{\pi}{4} = 3.46 \times 10^{-4} \text{ m}^2$$

Fluid velocity, total condensation

$$u_t = \frac{0.015}{931 \times 3.46 \times 10^{-4}} = 0.047 \text{ m/s}$$

$$Re = \frac{\rho u d_i}{\mu_L} = \frac{931 \times 0.047 \times 21 \times 10^{-3}}{0.21 \times 10^{-3}} = 4376$$

$$h'_i = 0.021 \times \frac{0.688}{21 \times 10^{-3}} (4376)^{0.8} (1.27)^{0.43} = 624 \text{ W/m}^2\text{°C} \quad (12.53)$$

$$h_c = 624 \left[ \frac{1 + \sqrt{931/1.65}}{2} \right] = 7723 \text{ W/m}^2\text{°C} \quad (12.54)$$

Take higher value,  $h_c = \underline{\underline{7723 \text{ W/m}^2\text{°C}}}$

### Example 12.6

It is proposed to use an existing distillation column, which is fitted with a dephlegmator (reflux condenser) which has 200 vertical, 50 mm i.d., tubes, for separating benzene from a mixture of chlorobenzenes. The top product will be 2500 kg/h benzene and the column will operate with a reflux ratio of 3. Check if the tubes are likely to flood. The condenser pressure will be 1 bar.

### Solution

The vapour will flow up and the liquid down the tubes. The maximum flow rates of both will occur at the base of the tube.

$$\text{Vapour flow} = (3 + 1)2500 = 10,000 \text{ kg/h}$$

$$\text{Liquid flow} = 3 \times 2500 = 7500 \text{ kg/h}$$

$$\text{Total area tubes} = \frac{\pi}{4} (50 \times 10^{-3})^2 \times 200 = 0.39 \text{ m}^2$$

Densities at benzene boiling point

$$\rho_L = 840 \text{ kg/m}^3, \quad \rho_v = 2.7 \text{ kg/m}^3$$

Vapour velocity (vapour flowing alone in tube)

$$u_v = \frac{10,000}{3600 \times 0.39 \times 2.7} = 2.64 \text{ m/s}$$

Liquid velocity (liquid alone)

$$u_L = \frac{7500}{3600 \times 0.39 \times 840} = 0.006 \text{ m/s}$$

From equation 12.55 for no flooding

$$[u_v^{1/2} \rho_v^{1/4} + u_L^{1/2} \rho_L^{1/4}] < 0.6 [g d_i (\rho_L - \rho_v)]^{1/4}$$

$$[(2.64)^{1/2}(2.7)^{1/4} + (0.006)^{1/2}(840)^{1/4}] < 0.6[9.81 \times 50 \times 10^{-3}(840 - 2.7)]^{1/4}$$

$$[2.50] < [2.70]$$

Tubes should not flood, but there is little margin of safety.

#### 12.10.4. Condensation inside horizontal tubes

Where condensation occurs in a horizontal tube the heat-transfer coefficient at any point along the tube will depend on the flow pattern at that point. The various patterns that can exist in two-phase flow are shown in Figure 12.44; and are discussed in Volume 1, Chapter 5. In condensation, the flow will vary from a single-phase vapour at the inlet to a single-phase liquid at the outlet; with all the possible patterns of flow occurring between these points. Bell *et al.* (1970) give a method for following the change in flow pattern as condensation occurs on a Baker flow-regime map. Correlations for estimating the average condensation coefficient have been published by several workers, but there is no generally satisfactory method that will give accurate predictions over a wide flow range. A comparison of the published methods is given by Bell *et al.* (1970).

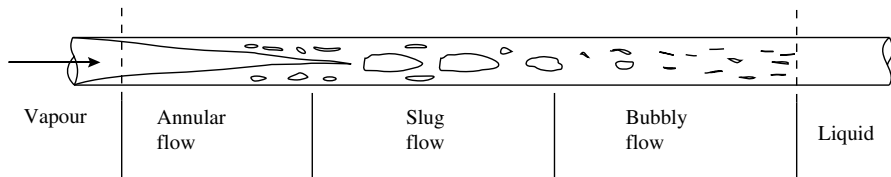


Figure 12.44. Flow patterns, vapour condensing in a horizontal tube

Two flow models are used to estimate the mean condensation coefficient in horizontal tubes: stratified flow, Figure 12.45a, and annular flow, Figure 12.45b. The stratified flow model represents the limiting condition at low condensate and vapour rates, and the annular model the condition at high vapour and low condensate rates. For the stratified flow model, the condensate film coefficient can be estimated from the Nusselt equation, applying a suitable correction for the reduction in the coefficient caused by



Figure 12.45. Flow patterns in condensation. (a) Stratified flow (b) Annular flow

the accumulation of condensate in the bottom of the tube. The correction factor will typically be around 0.8, so the coefficient for stratified flow can be estimated from:

$$(h_c)_s = 0.76k_L \left[ \frac{\rho_L(\rho_L - \rho_v)g}{\mu_L \Gamma_h} \right]^{1/3} \quad (12.56)$$

The Boyko-Kruzhilin equation, equation 12.52, can be used to estimate the coefficient for annular flow.

For condenser design, the mean coefficient should be evaluated using the correlations for both annular and stratified flow and the *higher* value selected.

### 12.10.5. Condensation of steam

Steam is frequently used as a heating medium. The film coefficient for condensing steam can be calculated using the methods given in the previous sections; but, as the coefficient will be high and will rarely be the limiting coefficient, it is customary to assume a typical, conservative, value for design purposes. For air-free steam a coefficient of  $8000 \text{ W/m}^2\text{C}$  ( $1500 \text{ Btu/h ft}^2\text{F}$ ) can be used.

### 12.10.6. Mean temperature difference

A pure, saturated, vapour will condense at a fixed temperature, at constant pressure. For an isothermal process such as this, the simple logarithmic mean temperature difference can be used in the equation 12.1; no correction factor for multiple passes is needed. The logarithmic mean temperature difference will be given by:

$$\Delta T_{\text{lm}} = \frac{(t_2 - t_1)}{\ln \left[ \frac{T_{\text{sat}} - t_1}{T_{\text{sat}} - t_2} \right]} \quad (12.57)$$

where  $T_{\text{sat}}$  = saturation temperature of the vapour,

$t_1$  = inlet coolant temperature,

$t_2$  = outlet coolant.

When the condensation process is not exactly isothermal but the temperature change is small; such as where there is a significant change in pressure, or where a narrow boiling range multicomponent mixture is being condensed; the logarithmic temperature difference can still be used but the temperature correction factor will be needed for multipass condensers. The appropriate terminal temperatures should be used in the calculation.

### 12.10.7. Desuperheating and sub-cooling

When the vapour entering the condenser is superheated, and the condensate leaving the condenser is cooled below its boiling point (sub-cooled), the temperature profile will be as shown in Figure 12.46.

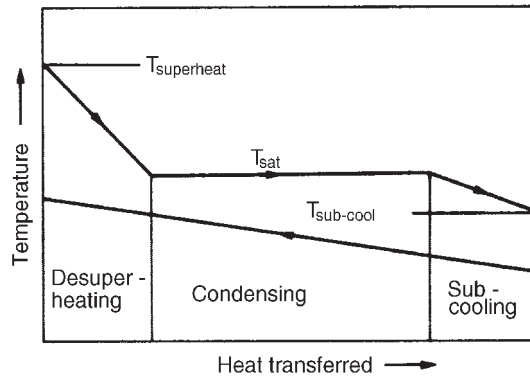


Figure 12.46. Condensation with desuperheating and sub-cooling

### ***Desuperheating***

If the degree of superheat is large, it will be necessary to divide the temperature profile into sections and determine the mean temperature difference and heat-transfer coefficient separately for each section. If the tube wall temperature is below the dew point of the vapour, liquid will condense directly from the vapour on to the tubes. In these circumstances it has been found that the heat-transfer coefficient in the superheating section is close to the value for condensation and can be taken as the same. So, where the amount of superheating is not too excessive, say less than 25 per cent of the latent heat load, and the outlet coolant temperature is well below the vapour dew point, the sensible heat load for desuperheating can be lumped with the latent heat load. The total heat-transfer area required can then be calculated using a mean temperature difference based on the saturation temperature (not the superheat temperature) and the estimated condensate film heat-transfer coefficient.

### ***Sub-cooling of condensate***

Some sub-cooling of the condensate will usually be required to control the net positive suction head at the condensate pump (see Chapter 5, and Volume 1, Chapter 8), or to cool a product for storage. Where the amount of sub-cooling is large, it is more efficient to sub-cool in a separate exchanger. A small amount of sub-cooling can be obtained in a condenser by controlling the liquid level so that some part of the tube bundle is immersed in the condensate.

In a horizontal shell-side condenser a dam baffle can be used, Figure 12.47*a*. A vertical condenser can be operated with the liquid level above the bottom tube sheet, Figure 12.47*b*.

The temperature difference in the sub-cooled region will depend on the degree of mixing in the pool of condensate. The limiting conditions are plug flow and complete mixing. The temperature profile for plug flow is that shown in Figure 12.46. If the pool is perfectly mixed, the condensate temperature will be constant over the sub-cooling region and equal to the condensate outlet temperature. Assuming perfect mixing will give a very

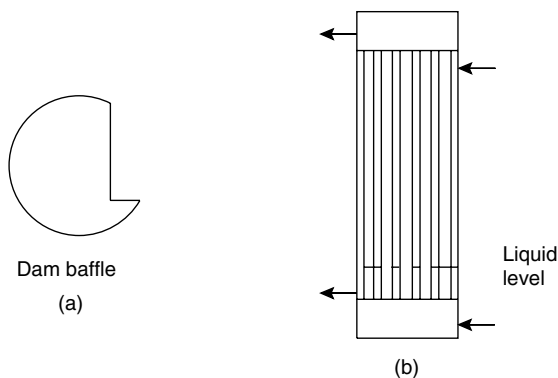


Figure 12.47. Arrangements for sub-cooling

conservative (safe) estimate of the mean temperature difference. As the liquid velocity will be low in the sub-cooled region the heat-transfer coefficient should be estimated using correlations for natural convection (see Volume 1, Chapter 9); a typical value would be  $200 \text{ W/m}^2\text{°C}$ .

### 12.10.8. Condensation of mixtures

The correlations given in the previous sections apply to the condensation of a single component; such as an essentially pure overhead product from a distillation column. The design of a condenser for a mixture of vapours is a more difficult task.

The term “mixture of vapours” covers three related situations of practical interest:

1. Total condensation of a multicomponent mixture; such as the overheads from a multicomponent distillation.
2. Condensation of only part of a multicomponent vapour mixture, all components of which are theoretically condensable. This situation will occur where the dew point of some of the lighter components is above the coolant temperature. The uncondensed component may be soluble in the condensed liquid; such as in the condensation of some hydrocarbons mixtures containing light “gaseous” components.
3. Condensation from a non-condensable gas, where the gas is not soluble to any extent in the liquid condensed. These exchangers are often called cooler-condensers.

The following features, common to all these situations, must be considered in the developing design methods for mixed vapour condensers:

1. The condensation will not be isothermal. As the heavy component condenses out the composition of the vapour, and therefore its dew point, change.
2. Because the condensation is not isothermal there will be a transfer of sensible heat from the vapour to cool the gas to the dew point. There will also be a transfer of sensible heat from the condensate, as it must be cooled from the temperature at which it condensed to the outlet temperature. The transfer of sensible heat from the



vapour can be particularly significant, as the sensible-heat transfer coefficient will be appreciably lower than the condensation coefficient.

3. As the composition of the vapour and liquid change throughout the condenser their physical properties vary.
4. The heavy component must diffuse through the lighter components to reach the condensing surface. The rate of condensation will be governed by the rate of diffusion, as well as the rate of heat transfer.

### Temperature profile

To evaluate the true temperature difference (driving force) in a mixed vapour condenser a condensation curve (temperature vs. enthalpy diagram) must be calculated; showing the change in vapour temperature versus heat transferred throughout the condenser, Figure 12.48. The temperature profile will depend on the liquid-flow pattern in the condenser. There are two limiting conditions of condensate-vapour flow:

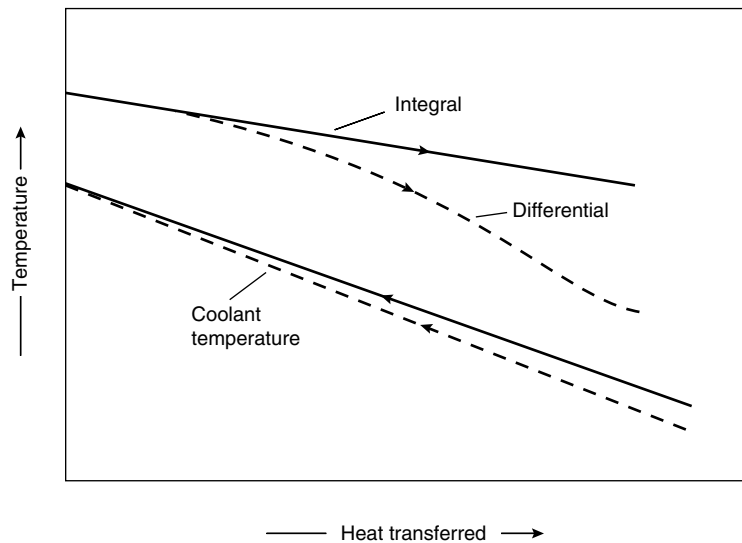


Figure 12.48. Condensation curves

1. Differential condensation: in which the liquid separates from the vapour from which it has condensed. This process is analogous to differential, or Rayleigh, distillation, and the condensation curve can be calculated using methods similar to those for determining the change in composition in differential distillation; see Volume 2, Chapter 11.
2. Integral condensation: in which the liquid remains in equilibrium with the uncondensed vapour. The condensation curve can be determined using procedures similar to those for multicomponent flash distillation given in Chapter 11. This will be a relatively simple calculation for a binary mixture, but complex and tedious for mixtures of more than two components.

It is normal practice to assume that integral condensation occurs. The conditions for integral condensation will be approached if condensation is carried out in one pass, so that the liquid and vapour follow the same path; as in a vertical condenser with condensation inside or outside the tubes. In a horizontal shell-side condenser the condensate will tend to separate from the vapour. The mean temperature difference will be lower for differential condensation, and arrangements where liquid separation is likely to occur should generally be avoided for the condensation of mixed vapours.

Where integral condensation can be considered to occur, the use of a corrected logarithmic mean temperature difference based on the terminal temperatures will generally give a conservative (safe) estimate of the mean temperature difference, and can be used in preliminary design calculations.

### ***Estimation of heat-transfer coefficients***

*Total condensation.* For the design of a multicomponent condenser in which the vapour is totally condensed, an estimate of the mean condensing coefficient can be made using the single component correlations with the liquid physical properties evaluated at the average condensate composition. It is the usual practice to apply a factor of safety to allow for the sensible-heat transfer and any resistance to mass transfer. Frank (1978) suggests a factor of 0.65, but this is probably too pessimistic. Kern (1950) suggests increasing the area calculated for condensation alone by the ratio of the total heat (condensing + sensible) to the condensing load. Where a more exact estimate of the coefficient is required, and justified by the data, the rigorous methods developed for partial condensation can be used.

*Partial condensation.* The methods developed for partial condensation and condensation from a non-condensable gas can be divided into two classes:

1. Empirical methods: approximate methods, in which the resistance to heat transfer is considered to control the rate of condensation, and the mass transfer resistance is neglected. Design methods have been published by Silver (1947), Bell and Ghaly (1973) and Ward (1960).
2. Analytical methods: more exact procedures, which are based on some model of the heat and mass transfer process, and which take into account the diffusional resistance to mass transfer. The classic method is that of Colburn and Hougen (1934); see also Colburn and Drew (1937) and Porter and Jeffreys (1963). The analytical methods are complex, requiring step-by-step, trial and error, calculations, or graphical procedures. They are suited for computer solution using numerical methods; and proprietary design programs are available. Examples of the application of the Colburn and Drew method are given by Kern (1950) and Jeffreys (1961). The method is discussed briefly in Volume 1, Chapter 9.

An assessment of the methods available for the design of condensers where the condensation is from a non-condensable gas is given by McNaught (1983).

*Approximate methods.* The local coefficient for heat transfer can be expressed in terms of the local condensate film coefficient  $h'_c$  and the local coefficient for sensible-heat

transfer from the vapour (the gas film coefficient)  $h'_g$ , by a relationship first proposed by Silver (1947):

$$\frac{1}{h'_{cg}} = \frac{1}{h'_c} + \frac{Z}{h'_g} \quad (12.58)$$

where  $h'_{cg}$  = the local effective cooling-condensing coefficient

and 
$$Z = \frac{\Delta H_s}{\Delta H_t} = x C_{pg} \frac{dT}{dH_t},$$

( $\Delta H_s/\Delta H_t$ ) = the ratio of the change in sensible heat to the total enthalpy change.

( $dT/dH_t$ ) = slope of the temperature–enthalpy curve,

$x$  = vapour quality, mass fraction of vapour,

$C_{pg}$  = vapour (gas) specific heat.

The term  $dT/dH_t$  can be evaluated from the condensation curve;  $h'_c$  from the single component correlations; and  $h'_g$  from correlations for forced convection.

If this is done at several points along the condensation curve the area required can be determined by graphical or numerical integration of the expression:

$$A = \int_0^{Q_t} \frac{dQ}{U(T_v - t_c)} \quad (12.59)$$

where  $Q_t$  = total heat transferred,

$U$  = overall heat transfer coefficient, from equation 12.1, using  $h'_{cg}$ ,

$T_v$  = local vapour (gas) temperature,

$t_c$  = local cooling medium temperature.

Gilmore (1963) gives an integrated form of equation 12.57, which can be used for the approximate design of partial condensers

$$\frac{1}{h_{cg}} = \frac{1}{h_c} + \frac{Q_g}{Q_t} \frac{1}{h_g} \quad (12.60)$$

where  $h_{cg}$  = mean effective coefficient,

$h_c$  = mean condensate film coefficient, evaluated from the single-component correlations, at the average condensate composition, and total condensate loading,

$h_g$  = mean gas film coefficient, evaluated using the average vapour flow-rate : arithmetic mean of the inlet and outlet vapour (gas) flow-rates,

$Q_g$  = total sensible-heat transfer from vapour (gas),

$Q_t$  = total heat transferred: latent heat of condensation + sensible heat for cooling the vapour (gas) and condensate.

As a rough guide, the following rules of thumb suggested by Frank (1978) can be used to decide the design method to use for a partial condenser (cooler-condenser):

1. Non-condensables <0.5 per cent: use the methods for total condensation; ignore the presence of the uncondensed portion.

2. Non-condensables >70 per cent: assume the heat transfer is by forced convection only. Use the correlations for forced convection to calculate the heat-transfer coefficient, but include the latent heat of condensation in the total heat load transferred.
3. Between 0.5 to 70 per cent non-condensables: use methods that consider both mechanisms of heat transfer.

In partial condensation it is usually better to put the condensing stream on the shell-side, and to select a baffle spacing that will maintain high vapour velocities, and therefore high sensible-heat-transfer coefficients.

*Fog formation.* In the condensation of a vapour from a non-condensable gas, if the bulk temperature of the gas falls below the dew point of the vapour, liquid can condense out directly as a mist or fog. This condition is undesirable, as liquid droplets may be carried out of the condenser. Fog formation in cooler-condensers is discussed by Colburn and Edison (1941) and Lo Pinto (1982). Steinmeyer (1972) gives criteria for the prediction of fog formation. Demisting pads can be used to separate entrained liquid droplets.

### 12.10.9. Pressure drop in condensers

The pressure drop on the condensing side is difficult to predict as two phases are present and the vapour mass velocity is changing throughout the condenser.

A common practice is to calculate the pressure drop using the methods for single-phase flow and apply a factor to allow for the change in vapour velocity. For total condensation, Frank (1978) suggests taking the pressure drop as 40 per cent of the value based on the inlet vapour conditions; Kern (1950) suggests a factor of 50 per cent.

An alternative method, which can also be used to estimate the pressure drop in a partial condenser, is given by Gloyer (1970). The pressure drop is calculated using an average vapour flow-rate in the shell (or tubes) estimated as a function of the ratio of the vapour flow-rate in and out of the shell (or tubes), and the temperature profile.

$$W_s \text{ (average)} = W_s \text{ (inlet)} \times K_2 \quad (12.61)$$

$K_2$  is obtained from Figure 12.49.

$\Delta T_{\text{in}}/\Delta T_{\text{out}}$  in Figure 12.49 is the ratio of the terminal temperature differences.

These methods can be used to make a crude estimate of the likely pressure drop. A reliable prediction can be obtained by treating the problem as one of two-phase flow. For tube-side condensation the general methods for two-phase flow in pipes can be used; see Collier and Thome (1994); and Volume 1, Chapter 5. As the flow pattern will be changing throughout condensation, some form of step-wise procedure will need to be used. Two-phase flow on the shell-side is discussed by Grant (1973), who gives a method for predicting the pressure drop based on Tinker's shell-side flow model.

A method for estimating the pressure drop on the shell-side of horizontal condensers is given in the Engineering Sciences Data Unit Design Guide, ESDU 84023 (1985).

Pressure drop is only likely to be a major consideration in the design of vacuum condensers; and where reflux is returned to a column by gravity flow from the condenser.

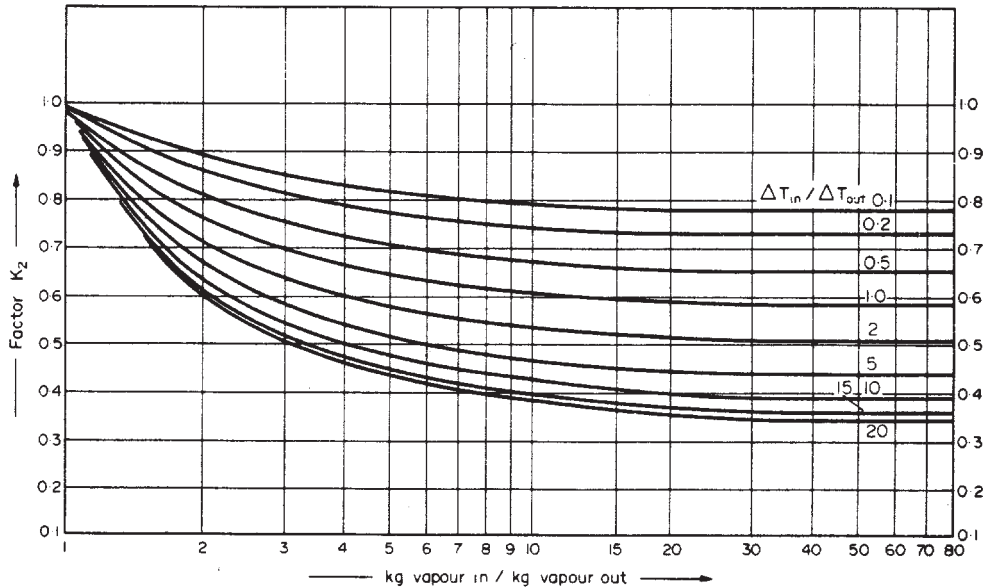


Figure 12.49. Factor for average vapour flow-rate for pressure-drop calculation (Gloyer, 1970)

### Example 12.7

Design a condenser for the following duty: 45,000 kg/h of mixed light hydrocarbon vapours to be condensed. The condenser to operate at 10 bar. The vapour will enter the condenser saturated at 60°C and the condensation will be complete at 45°C. The average molecular weight of the vapours is 52. The enthalpy of the vapour is 596.5 kJ/kg and the condensate 247.0 kJ/kg. Cooling water is available at 30°C and the temperature rise is to be limited to 10°C. Plant standards require tubes of 20 mm o.d., 16.8 mm i.d., 4.88 m (16 ft) long, of admiralty brass. The vapours are to be totally condensed and no sub-cooling is required.

### Solution

Only the thermal design will be done. The physical properties of the mixture will be taken as the mean of those for n-propane (MW = 44) and n-butane (MW = 58), at the average temperature.

$$\text{Heat transferred from vapour} = \frac{45,000}{3600}(596.5 - 247.0) = 4368.8 \text{ kW}$$

$$\text{Cooling water flow} = \frac{4368.8}{(40 - 30)4.18} = \underline{\underline{104.5 \text{ kg/s}}}$$

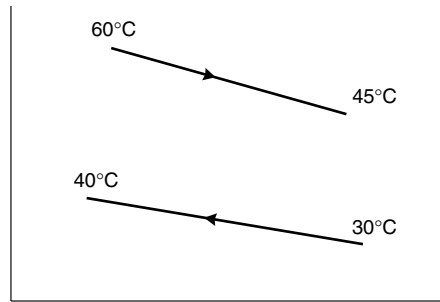
$$\text{Assumed overall coefficient (Table 12.1)} = 900 \text{ W/m}^2\text{°C}$$

Mean temperature difference: the condensation range is small and the change in saturation temperature will be linear, so the corrected logarithmic mean temperature

difference can be used.

$$R = \frac{(60 - 45)}{(40 - 30)} = 1.5 \quad (12.6)$$

$$S = \frac{(40 - 30)}{(60 - 30)} = 0.33 \quad (12.7)$$



Try a horizontal exchanger, condensation in the shell, four tube passes. For one shell pass, four tube passes, from Figure 12.19,  $F_t = 0.92$

$$\Delta T_{lm} = \frac{(60 - 40) - (45 - 30)}{\ln \frac{(60 - 40)}{(45 - 30)}} = 17.4^\circ\text{C}$$

$$\Delta T_m = 0.92 \times 17.4 = 16^\circ\text{C}$$

$$\text{Trial area} = \frac{4368.8 \times 10^3}{900 \times 16} = 303 \text{ m}^2$$

Surface area of one tube =  $20 \times 10^{-3} \pi \times 4.88 = 0.305 \text{ m}^2$  (ignore tube sheet thickness)

$$\text{Number of tubes} = \frac{303}{0.305} = 992$$

Use square pitch,  $P_t = 1.25 \times 20 \text{ mm} = 25 \text{ mm}$ .

Tube bundle diameter

$$D_b = 20 \left( \frac{992}{0.158} \right)^{1/2.263} = 954 \text{ mm} \quad (12.3b)$$

Number of tubes in centre row  $N_r = D_b/P_t = 954/25 = 38$

### Shell-side coefficient

Estimate tube wall temperature,  $T_w$ ; assume condensing coefficient of  $1500 \text{ W/m}^2\text{°C}$ ,

Mean temperature

$$\text{Shell-side} = \frac{60 + 45}{2} = 52.5^\circ\text{C}$$

$$\text{Tube-side} = \frac{40 + 30}{2} = 35^\circ\text{C}$$

$$(52.5 - T_w)1500 = (52.5 - 35)900$$

$$T_w = 42.0^\circ\text{C}$$

$$\text{Mean temperature condensate} = \frac{52.5 + 42.0}{2} = 47^\circ\text{C}$$

Physical properties at  $47^\circ\text{C}$

$$\mu_L = 0.16 \text{ mNs/m}^2$$

$$\rho_L = 551 \text{ kg/m}^3$$

$$k_L = 0.13 \text{ W/m}^\circ\text{C}$$

vapour density at mean vapour temperature

$$\rho_v = \frac{52}{22.4} \times \frac{273}{(273 + 52.5)} \times \frac{10}{1} = 19.5 \text{ kg/m}^3$$

$$\Gamma_h = \frac{W_c}{LN_t} = \frac{45,000}{3600} \times \frac{1}{4.88 \times 992} = 2.6 \times 10^{-3} \text{ kg/s m}$$

$$N_r = \frac{2}{3} \times 38 = 25$$

$$h_c = 0.95 \times 0.13 \left[ \frac{551(551 - 19.5)9.81}{0.16 \times 10^{-3} \times 2.6 \times 10^{-3}} \right]^{1/3} \times 25^{-1/6} \quad (12.50)$$

$$= 1375 \text{ W/m}^2\text{C}$$

Close enough to assumed value of  $1500 \text{ W/m}^2\text{C}$ , so no correction to  $T_w$  needed.

### **Tube-side coefficient**

$$\text{Tube cross-sectional area} = \frac{\pi}{4}(16.8 \times 10^{-3})^2 \times \frac{992}{4} = 0.055 \text{ m}^2$$

Density of water, at  $35^\circ\text{C} = 993 \text{ kg/m}^3$

$$\text{Tube velocity} = \frac{104.5}{993} \times \frac{1}{0.055} = 1.91 \text{ m/s}$$

$$h_i = \frac{4200(1.35 + 0.02 \times 35)1.91^{0.8}}{16.8^{0.2}} \quad (12.17)$$

$$= 8218 \text{ W/m}^2\text{C}$$

Fouling factors: as neither fluid is heavily fouling, use  $6000 \text{ W/m}^2\text{C}$  for each side.

$$k_w = 50 \text{ W/m}^\circ\text{C}$$

### **Overall coefficient**

$$\frac{1}{U} = \frac{1}{1375} + \frac{1}{6000} + \frac{20 \times 10^{-3} \ln \left( \frac{20}{16.8} \right)}{2 \times 50} + \frac{20}{16.8} \times \frac{1}{6000} + \frac{20}{16.8} \times \frac{1}{8218}$$

$$U = \underline{\underline{786 \text{ W/m}^2\text{C}}} \quad (12.2)$$

Significantly lower than the assumed value of  $900 \text{ W/m}^2\text{°C}$ .  
Repeat calculation using new trial value of  $750 \text{ W/m}^2\text{°C}$ .

$$\begin{aligned}\text{Area} &= \frac{4368 \times 10^3}{750 \times 16} = 364 \text{ m}^2 \\ \text{Number of tubes} &= \frac{364}{0.305} = 1194 \\ D_b &= 20 \left( \frac{1194}{0.158} \right)^{1/2.263} = 1035 \text{ mm}\end{aligned}\quad (12.36)$$

$$\text{Number of tubes in centre row} = \frac{1035}{25} = 41$$

$$\Gamma_h = \frac{45,000}{3600} \times \frac{1}{4.88 \times 1194} = 2.15 \times 10^{-3} \text{ kg/m s}$$

$$N_r = \frac{2}{3} \times 41 = 27$$

$$\begin{aligned}h_c &= 0.95 \times 0.13 \left[ \frac{551(551 - 19.5)9.81}{0.16 \times 10^{-3} \times 2.15 \times 10^{-3}} \right]^{1/3} \times 27^{-1/6} \\ &= 1447 \text{ W/m}^2\text{°C}\end{aligned}\quad (12.50)$$

$$\text{New tube velocity} = 1.91 \times \frac{992}{1194} = 1.59 \text{ m/s}$$

$$h_i = 4200(1.35 + 0.02 \times 35) \frac{1.59^{0.8}}{16.8^{0.2}} = 7097 \text{ W/m}^2\text{°C}\quad (12.17)$$

$$\begin{aligned}\frac{1}{U} &= \frac{1}{1447} + \frac{1}{6000} + \frac{20 \times 10^{-3} \ln \left( \frac{20}{16.8} \right)}{2 \times 50} \\ &\quad + \frac{20}{16.8} \times \frac{1}{6000} + \frac{20}{16.8} \times \frac{1}{7097} \\ U &= \underline{\underline{773 \text{ W/m}^2\text{°C}}}\end{aligned}\quad (12.2)$$

Close enough to estimate, firm up design.

### **Shell-side pressure drop**

Use pull-through floating head, no need for close clearance.

Select baffle spacing = shell diameter, 45 per cent cut.

From Figure 12.10, clearance = 95 mm.

$$\text{Shell i.d.} = 1035 + 95 = 1130 \text{ mm}$$

Use Kern's method to make an approximate estimate.

$$\begin{aligned}\text{Cross-flow area } A_s &= \frac{(25 - 20)}{25} 1130 \times 1130 \times 10^{-6} \\ &= 0.255 \text{ m}^2\end{aligned}\quad (12.21)$$



Mass flow-rate, based on inlet conditions

$$G_s = \frac{45,000}{3600} \times \frac{1}{0.255} = 49.02 \text{ kg/s m}^2$$

$$\begin{aligned} \text{Equivalent diameter, } d_e &= \frac{1.27}{20} (25^2 - 0.785 \times 20^2) \\ &= 19.8 \text{ mm} \end{aligned} \quad (12.22)$$

$$\text{Vapour viscosity} = 0.008 \text{ mNs/m}^2$$

$$Re = \frac{49.02 \times 19.8 \times 10^{-3}}{0.008 \times 10^{-3}} = 121,325$$

From Figure 12.30,  $j_f = 2.2 \times 10^{-2}$

$$u_s = \frac{G_s}{\rho_v} = \frac{49.02}{19.5} = 2.51 \text{ m/s}$$

Take pressure drop as 50 per cent of that calculated using the inlet flow; neglect viscosity correction.

$$\begin{aligned} \Delta P_s &= \frac{1}{2} \left[ 8 \times 2.2 \times 10^{-2} \left( \frac{1130}{19.8} \right) \left( \frac{4.88}{1.130} \right) \frac{19.5(2.51)^2}{2} \right] \\ &= 1322 \text{ N/m}^2 \\ &= \underline{\underline{1.3 \text{ kPa}}} \end{aligned} \quad (12.26)$$

Negligible; more sophisticated method of calculation not justified.

### ***Tube-side pressure drop***

$$\text{Viscosity of water} = 0.6 \text{ mN s/m}^2$$

$$Re = \frac{u_t \rho d_i}{\mu} = \frac{1.59 \times 993 \times 16.8 \times 10^{-3}}{0.6 \times 10^{-3}} = \underline{\underline{44,208}}$$

From Figure 12.24,  $j_f = 3.5 \times 10^{-3}$ .

Neglect viscosity correction.

$$\begin{aligned} \Delta P_t &= 4 \left[ 8 \times 3.5 \times 10^{-3} \left( \frac{4.88}{16.8 \times 10^{-3}} \right) + 2.5 \right] \frac{993 \times 1.59^2}{2} \\ &= 53,388 \text{ N/m}^2 \\ &= \underline{\underline{53 \text{ kPa}}} \text{ (7.7 psi)}, \end{aligned} \quad (12.20)$$

acceptable.

## **12.11. REBOILERS AND VAPORISERS**

The design methods given in this section can be used for reboilers and vaporisers. Reboilers are used with distillation columns to vaporise a fraction of the bottom product; whereas in a vaporiser essentially all the feed is vaporised.

Three principal types of reboiler are used:

1. Forced circulation, Figure 12.50: in which the fluid is pumped through the exchanger, and the vapour formed is separated in the base of the column. When used as a vaporiser a disengagement vessel will have to be provided.

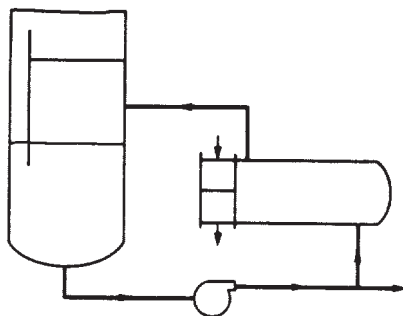


Figure 12.50. Forced-circulation reboiler

2. Thermosyphon, natural circulation, Figure 12.51: vertical exchangers with vaporisation in the tubes, or horizontal exchangers with vaporisation in the shell. The liquid circulation through the exchanger is maintained by the difference in density between the two-phase mixture of vapour and liquid in the exchanger and the single-phase liquid in the base of the column. As with the forced-circulation type, a disengagement vessel will be needed if this type is used as a vaporiser.
3. Kettle type, Figure 12.52: in which boiling takes place on tubes immersed in a pool of liquid; there is no circulation of liquid through the exchanger. This type is also, more correctly, called a submerged bundle reboiler. In some applications it is possible to accommodate the bundle in the base of the column, Figure 12.53; saving the cost of the exchanger shell.

### **Choice of type**

The choice of the best type of reboiler or vaporiser for a given duty will depend on the following factors:

1. The nature of the process fluid, particularly its viscosity and propensity to fouling.
2. The operating pressure: vacuum or pressure.
3. The equipment layout, particularly the headroom available.

Forced-circulation reboilers are especially suitable for handling viscous and heavily fouling process fluids; see Chantry and Church (1958). The circulation rate is predictable and high velocities can be used. They are also suitable for low vacuum operations, and for low rates of vaporisation. The major disadvantage of this type is that a pump is required and the pumping cost will be high. There is also the danger that leakage of hot fluid will occur at the pump seal; canned-rotor type pumps can be specified to avoid the possibility of leakage.

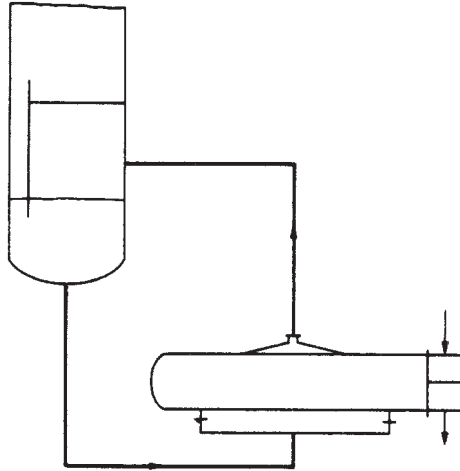


Figure 12.51. Horizontal thermosyphon reboiler

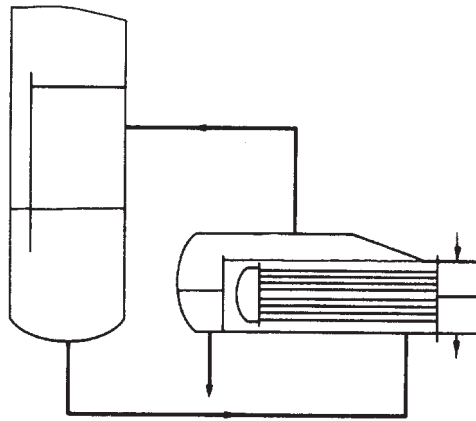


Figure 12.52. Kettle reboiler

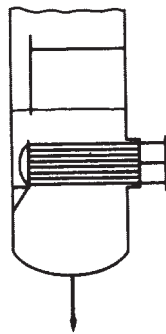


Figure 12.53. Internal reboiler

Thermosyphon reboilers are the most economical type for most applications, but are not suitable for high viscosity fluids or high vacuum operation. They would not normally be specified for pressures below 0.3 bar. A disadvantage of this type is that the column base must be elevated to provide the hydrostatic head required for the thermosyphon effect. This will increase the cost of the column supporting-structure. Horizontal reboilers require less headroom than vertical, but have more complex pipework. Horizontal exchangers are more easily maintained than vertical, as tube bundle can be more easily withdrawn.

Kettle reboilers have lower heat-transfer coefficients than the other types, as there is no liquid circulation. They are not suitable for fouling materials, and have a high residence time. They will generally be more expensive than an equivalent thermosyphon type as a larger shell is needed, but if the duty is such that the bundle can be installed in the column base, the cost will be competitive with the other types. They are often used as vaporisers, as a separate vapour-liquid disengagement vessel is not needed. They are suitable for vacuum operation, and for high rates of vaporisation, up to 80 per cent of the feed.

### 12.11.1. Boiling heat-transfer fundamentals

The complex phenomena involved in heat transfer to a boiling liquid are discussed in Volume 1, Chapter 9. A more detailed account is given by Collier and Thome (1994), Tong and Tang (1997) and Hsu and Graham (1976). Only a brief discussion of the subject will be given in this section: sufficient for the understanding of the design methods given for reboilers and vaporisers.

The mechanism of heat transfer from a submerged surface to a pool of liquid depends on the temperature difference between the heated surface and the liquid; Figure 12.54. At low-temperature differences, when the liquid is below its boiling point, heat is transferred by natural convection. As the surface temperature is raised incipient boiling occurs, vapour

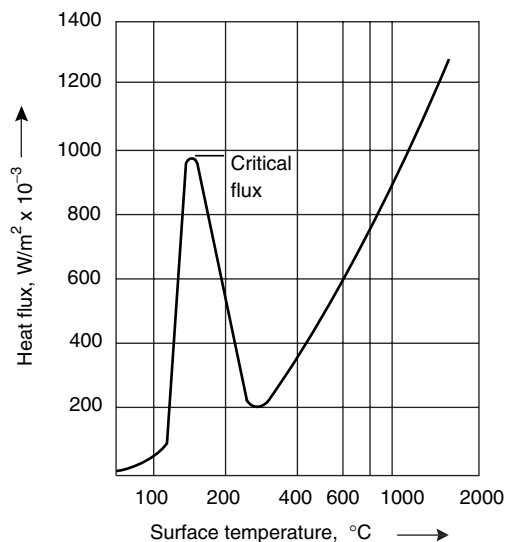


Figure 12.54. Typical pool boiling curve (water at 1 bar)

bubbles forming and breaking loose from the surface. The agitation caused by the rising bubbles, and other effects caused by bubble generation at the surface, result in a large increase in the rate of heat transfer. This phenomenon is known as nucleate boiling. As the temperature is raised further the rate of heat transfer increases until the heat flux reaches a critical value. At this point, the rate of vapour generation is such that dry patches occur spontaneously over the surface, and the rate of heat transfer falls off rapidly. At higher temperature differences, the vapour rate is such that the whole surface is blanketed with vapour, and the mechanism of heat transfer is by conduction through the vapour film. Conduction is augmented at high temperature differences by radiation.

The maximum heat flux achievable with nucleate boiling is known as the critical heat flux. In a system where the surface temperature is not self-limiting, such as a nuclear reactor fuel element, operation above the critical flux will result in a rapid increase in the surface temperature, and in the extreme situation the surface will melt. This phenomenon is known as “burn-out”. The heating media used for process plant are normally self-limiting; for example, with steam the surface temperature can never exceed the saturation temperature. Care must be taken in the design of electrically heated vaporisers to ensure that the critical flux can never be exceeded.

The critical flux is reached at surprisingly low temperature differences; around 20 to 30°C for water, and 20 to 50°C for light organics.

### ***Estimation of boiling heat-transfer coefficients***

In the design of vaporisers and reboilers the designer will be concerned with two types of boiling: pool boiling and convective boiling. Pool boiling is the name given to nucleate boiling in a pool of liquid; such as in a kettle-type reboiler or a jacketed vessel. Convective boiling occurs where the vaporising fluid is flowing over the heated surface, and heat transfer takes place both by forced convection and nucleate boiling; as in forced circulation or thermosyphon reboilers.

Boiling is a complex phenomenon, and boiling heat-transfer coefficients are difficult to predict with any certainty. Whenever possible experimental values obtained for the system being considered should be used, or values for a closely related system.

#### **12.11.2. Pool boiling**

In the nucleate boiling region the heat-transfer coefficient is dependent on the nature and condition of the heat-transfer surface, and it is not possible to present a universal correlation that will give accurate predictions for all systems. Palen and Taborek (1962) have reviewed the published correlations and compared their suitability for use in reboiler design.

The correlation given by Forster and Zuber (1955) can be used to estimate pool boiling coefficients, in the absence of experimental data. Their equation can be written in the form:

$$h_{nb} = 0.00122 \left[ \frac{k_L^{0.79} C_{PL}^{0.45} \rho_L^{0.49}}{\sigma^{0.5} \mu_L^{0.29} \lambda^{0.24} \rho_v^{0.24}} \right] (T_w - T_s)^{0.24} (p_w - p_s)^{0.75} \quad (12.62)$$

where  $h_{nb}$  = nucleate, pool, boiling coefficient,  $\text{W/m}^2\text{°C}$ ,

$k_L$  = liquid thermal conductivity,  $\text{W/m}^2\text{°C}$ ,

$C_{pL}$  = liquid heat capacity,  $\text{J/kg}^{\circ}\text{C}$ ,

$\rho_L$  = liquid density,  $\text{kg/m}^3$ ,

$\mu_L$  = liquid viscosity,  $\text{Ns/m}^2$ ,

$\lambda$  = latent heat,  $\text{J/kg}$ ,

$\rho_v$  = vapour density,  $\text{kg/m}^3$ ,

$T_w$  = wall, surface temperature,  $^{\circ}\text{C}$ ,

$T_s$  = saturation temperature of boiling liquid  $^{\circ}\text{C}$ ,

$p_w$  = saturation pressure corresponding to the wall temperature,  $T_w$ ,  $\text{N/m}^2$ ,

$p_s$  = saturation pressure corresponding to  $T_s$ ,  $\text{N/m}^2$ ,

$\sigma$  = surface tension,  $\text{N/m}$ .

The reduced pressure correlation given by Mostinski (1963) is simple to use and gives values that are as reliable as those given by more complex equations.

$$h_{nb} = 0.104(P_c)^{0.69}(q)^{0.7} \left[ 1.8 \left( \frac{P}{P_c} \right)^{0.17} + 4 \left( \frac{P}{P_c} \right)^{1.2} + 10 \left( \frac{P}{P_c} \right)^{10} \right] \quad (12.63)$$

where  $P$  = operating pressure, bar,

$P_c$  = liquid critical pressure, bar,

$q$  = heat flux,  $\text{W/m}^2$ .

*Note.*  $q = h_{nb}(T_w - T_s)$ .

Mostinski's equation is convenient to use when data on the fluid physical properties are not available.

Equations 12.62 and 12.63 are for boiling single component fluids; for mixtures the coefficient will generally be lower than that predicted by these equations. The equations can be used for close boiling range mixtures, say less than  $5^{\circ}\text{C}$ ; and for wider boiling ranges with a suitable factor of safety (see Section 12.11.6).

### Critical heat flux

It is important to check that the design, and operating, heat flux is well below the critical flux. Several correlations are available for predicting the critical flux. That given by Zuber *et al.* (1961) has been found to give satisfactory predictions for use in reboiler and vaporiser design. In SI units, Zuber's equation can be written as:

$$q_c = 0.131\lambda[\sigma g(\rho_L - \rho_v)\rho_v^2]^{1/4} \quad (12.64)$$

where  $q_c$  = maximum, critical, heat flux,  $\text{W/m}^2$ ,

$g$  = gravitational acceleration,  $9.81 \text{ m/s}^2$ .

Mostinski also gives a reduced pressure equation for predicting the maximum critical heat flux:

$$q_c = 3.67 \times 10^4 P_c \left( \frac{P}{P_c} \right)^{0.35} \left[ 1 - \left( \frac{P}{P_c} \right) \right]^{0.9} \quad (12.65)$$

### Film boiling

The equation given by Bromley (1950) can be used to estimate the heat-transfer coefficient for film boiling on tubes. Heat transfer in the film-boiling region will be controlled by conduction through the film of vapour, and Bromley's equation is similar to the Nusselt equation for condensation, where conduction is occurring through the film of condensate.

$$h_{fb} = 0.62 \left[ \frac{k_v^3 (\rho_L - \rho_v) \rho_v g \lambda}{\mu_v d_o (T_w - T_s)} \right]^{1/4} \quad (12.66)$$

where  $h_{fb}$  is the film boiling heat-transfer coefficient; the suffix  $v$  refers to the vapour phase and  $d_o$  is in metres. It must be emphasised that process reboilers and vaporisers will always be designed to operate in the nucleate boiling region. The heating medium would be selected, and its temperature controlled, to ensure that in operation the temperature difference is well below that at which the critical flux is reached. For instance, if direct heating with steam would give too high a temperature difference, the steam would be used to heat water, and hot water used as the heating medium.

### Example 12.8

Estimate the heat-transfer coefficient for the pool boiling of water at 2.1 bar, from a surface at 125°C. Check that the critical flux is not exceeded.

### Solution

Physical properties, from steam tables:

Saturation temperature,  $T_s = 121.8^\circ\text{C}$

$$\rho_L = 941.6 \text{ kg/m}^3, \quad \rho_v = 1.18 \text{ kg/m}^3$$

$$C_{pL} = 4.25 \times 10^3 \text{ J/kg}^\circ\text{C}$$

$$k_L = 687 \times 10^{-3} \text{ W/m}^\circ\text{C}$$

$$\mu_L = 230 \times 10^{-6} \text{ Ns/m}^2$$

$$\lambda = 2198 \times 10^3 \text{ J/kg}$$

$$\sigma = 55 \times 10^{-3} \text{ N/m}$$

$$p_w \text{ at } 125^\circ\text{C} = 2.321 \times 10^5 \text{ N/m}^2$$

$$p_s = 2.1 \times 10^5 \text{ N/m}^2$$

Use the Foster-Zuber correlation, equation 12.62:

$$\begin{aligned} h_b &= 1.22 \times 10^{-3} \left[ \frac{(687 \times 10^{-3})^{0.79} (4.25 \times 10^3)^{0.45} (941.6)^{0.49}}{(55 \times 10^{-3})^{0.5} (230 \times 10^{-6})^{0.29} (2198 \times 10^3)^{0.24} 1.18^{0.24}} \right] \\ &\quad \times (125 - 121.8)^{0.24} (2.321 \times 10^5 - 2.10 \times 10^5)^{0.75} \\ &= \underline{\underline{3738 \text{ W/m}^2^\circ\text{C}}} \end{aligned}$$

Use the Zuber correlation, equation 12.65:

$$q_c = 0.131 \times 2198 \times 10^3 [55 \times 10^{-3} \times 9.81(941.6 - 1.18)1.18^2]^{1/4}$$

$$= \underline{\underline{1.48 \times 10^6 \text{ W/m}^2}}$$

$$\text{Actual flux} = (125 - 121.8)3738 = \underline{\underline{11,962 \text{ W/m}^2}},$$

well below critical flux.

### 12.11.3. Convective boiling

The mechanism of heat transfer in convective boiling, where the boiling fluid is flowing through a tube or over a tube bundle, differs from that in pool boiling. It will depend on the state of the fluid at any point. Consider the situation of a liquid boiling inside a vertical tube; Figure 12.55. The following conditions occur as the fluid flows up the tube.

1. Single-phase flow region: at the inlet the liquid is below its boiling point (sub-cooled) and heat is transferred by forced convection. The equations for forced convection can be used to estimate the heat-transfer coefficient in this region.
2. Sub-cooled boiling: in this region the liquid next to the wall has reached boiling point, but not the bulk of the liquid. Local boiling takes place at the wall, which increases the rate of heat transfer over that given by forced convection alone.

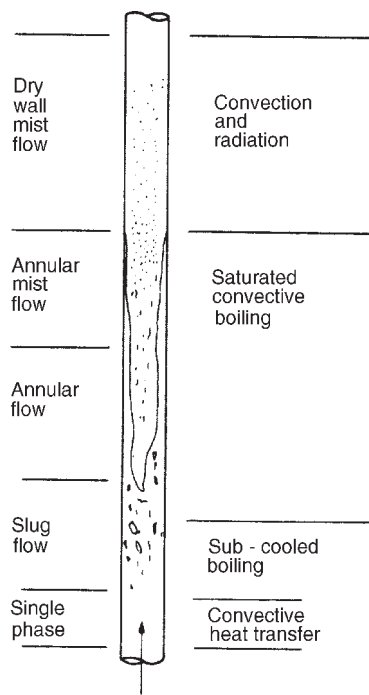


Figure 12.55. Convective boiling in a vertical tube



3. Saturated boiling region: in this region bulk boiling of the liquid is occurring in a manner similar to nucleate pool boiling. The volume of vapour is increasing and various flow patterns can form (see Volume 2, Chapter 14). In a long tube, the flow pattern will eventually become annular: where the liquid phase is spread over the tube wall and the vapour flows up the central core.
4. Dry wall region: Ultimately, if a large fraction of the feed is vaporised, the wall dries out and any remaining liquid is present as a mist. Heat transfer in this region is by convection and radiation to the vapour. This condition is unlikely to occur in commercial reboilers and vaporisers.

Saturated, bulk, boiling is the principal mechanism of interest in the design of reboilers and vaporisers.

A comprehensive review of the methods available for predicting convective boiling coefficients is given by Webb and Gupte (1992). The methods proposed by Chen (1966) and Shah (1976) are convenient to use in manual calculations and are accurate enough for preliminary design work. Chen's method is outlined below and illustrated in Example 12.9.

### **Chen's method**

In forced-convective boiling the effective heat-transfer coefficient  $h_{cb}$  can be considered to be made up of convective and nucleate boiling components;  $h'_{fc}$  and  $h'_{nb}$ .

$$h_{cb} = h'_{fc} + h'_{nb} \quad (12.67)$$

The convective boiling coefficient  $h'_{fc}$  can be estimated using the equations for single-phase forced-convection heat transfer modified by a factor  $f_c$  to account for the effects of two-phase flow:

$$h'_{fc} = h_{fc} \times f_c \quad (12.68)$$

The forced-convection coefficient  $h_{fc}$  is calculated assuming that the liquid phase is flowing in the conduit alone.

The two-phase correction factor  $f_c$  is obtained from Figure 12.56; in which the term  $1/X_{tt}$  is the Lockhart-Martinelli two-phase flow parameter with turbulent flow in both phases (See Volume 1, Chapter 5). This parameter is given by:

$$\frac{1}{X_{tt}} = \left[ \frac{x}{1-x} \right]^{0.9} \left[ \frac{\rho_L}{\rho_v} \right]^{0.5} \left[ \frac{\mu_v}{\mu_L} \right]^{0.1} \quad (12.69)$$

where  $x$  is the vapour quality, the mass fraction of vapour.

The nucleate boiling coefficient can be calculated using correlations for nucleate pool boiling modified by a factor  $f_s$  to account for the fact that nucleate boiling is more difficult in a flowing liquid.

$$h'_{nb} = h_{nb} \times f_s \quad (12.70)$$

The suppression factor  $f_s$  is obtained from Figure 12.57. It is a function of the liquid Reynolds number  $Re_L$  and the forced-convection correction factor  $f_c$ .

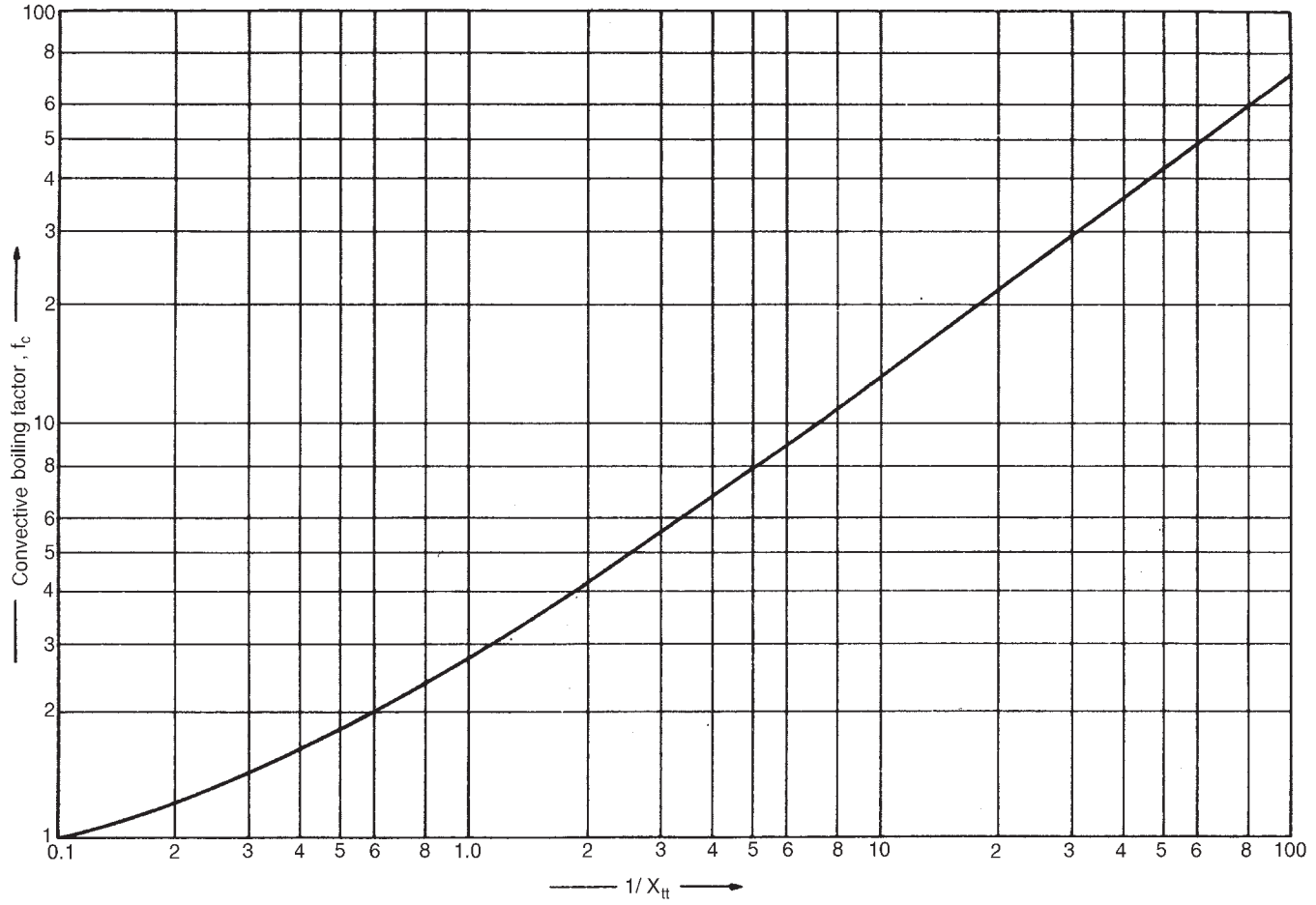


Figure 12.56. Convective boiling enhancement factor

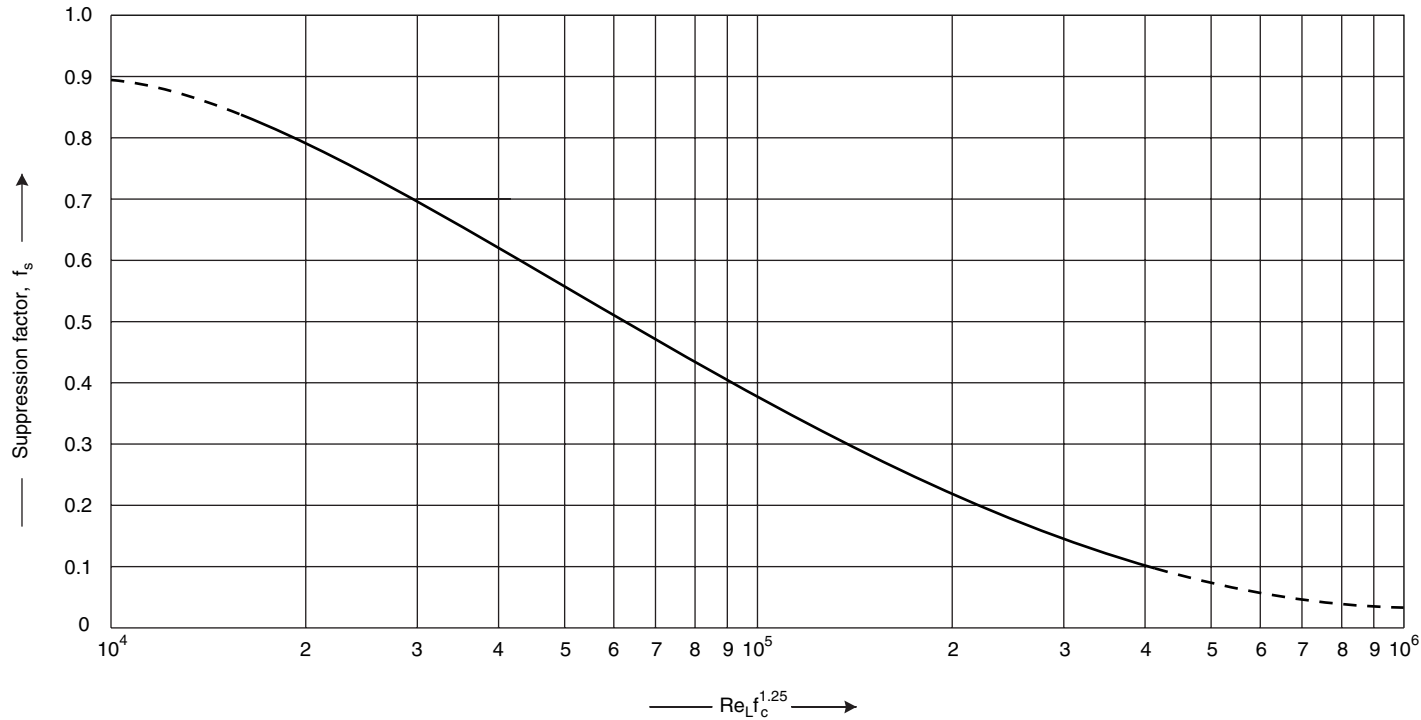


Figure 12.57. Nucleate boiling suppression factor

$Re_L$  is evaluated assuming that only the liquid phase is flowing in the conduit, and will be given by:

$$Re_L = \frac{(1-x)Gd_e}{\mu_L} \quad (12.71)$$

where  $G$  is the total mass flow rate per unit flow area.

Chen's method was developed from experimental data on forced convective boiling in vertical tubes. It can be applied, with caution, to forced convective boiling in horizontal tubes, and annular conduits (concentric pipes). Butterworth (1977) suggests that, in the absence of more reliable methods, it may be used to estimate the heat-transfer coefficient for forced convective boiling in cross-flow over tube bundles; using a suitable cross-flow correlation to predict the forced-convection coefficient. Shah's method was based on data for flow in horizontal and vertical tubes and annuli.

A major problem that will be encountered when applying convective boiling correlations to the design of reboilers and vaporisers is that, because the vapour quality changes progressively throughout the exchanger, a step-by-step procedure will be needed. The exchanger must be divided into sections and the coefficient and heat transfer area estimated sequentially for each section.

### Example 12.9

A fluid whose properties are essentially those of o-dichlorobenzene is vaporised in the tubes of a forced convection reboiler. Estimate the local heat-transfer coefficient at a point where 5 per cent of the liquid has been vaporised. The liquid velocity at the tube inlet is 2 m/s and the operating pressure is 0.3 bar. The tube inside diameter is 16 mm and the local wall temperature is estimated to be 120°C.

### Solution

Physical properties:

boiling point 136°C

$$\rho_L = 1170 \text{ kg/m}^3$$

$$\mu_L = 0.45 \text{ mNs/m}^2$$

$$\mu_v = 0.01 \text{ mNs/m}^2$$

$$\rho_v = 1.31 \text{ kg/m}^3$$

$$k_L = 0.11 \text{ W/m}^\circ\text{C}$$

$$C_{pL} = 1.25 \text{ kJ/kg}^\circ\text{C}$$

$$P_c = 41 \text{ bar}$$

The forced-convective boiling coefficient will be estimated using Chen's method.

With 5 per cent vapour, liquid velocity (for liquid flow in tube alone)

$$= 2 \times 0.95 = 1.90 \text{ m/s}$$

$$Re_L = \frac{1170 \times 1.90 \times 16 \times 10^{-3}}{0.45 \times 10^{-3}} = 79,040$$

From Figure 12.23,  $j_h = 3.3 \times 10^{-3}$

$$Pr = \frac{1.25 \times 10^3 \times 0.45 \times 10^{-3}}{0.11} = 5.1$$

Neglect viscosity correction term.

$$h_{fc} = \frac{0.11}{16 \times 10^{-3}} \times 3.3 \times 10^{-3} (79,040)(5.1)^{0.33} \quad (12.15)$$

$$= 3070 \text{ W/m}^2\text{°C}$$

$$\frac{1}{X_{tt}} = \left[ \frac{0.05}{1 - 0.05} \right]^{0.9} \left[ \frac{1170}{1.31} \right]^{0.5} \left[ \frac{0.01 \times 10^{-3}}{0.45 \times 10^{-3}} \right]^{0.1} \quad (12.69)$$

$$= 1.44$$

From Figure 12.56,  $f_c = 3.2$

$$h'_{fc} = 3.2 \times 3070 = 9824 \text{ W/m}^2\text{°C}$$

Using Mostinski's correlation to estimate the nucleate boiling coefficient

$$h_{nb} = 0.104 \times 41^{0.69} [h_{nb}(136 - 120)]^{0.7} \quad (12.63)$$

$$\times \left[ 1.8 \left( \frac{0.3}{41} \right)^{0.17} + 4 \left( \frac{0.3}{41} \right)^{1.2} + 10 \left( \frac{0.3}{41} \right)^{10} \right]$$

$$h_{nb} = 7.43 h_{nb}^{0.7}$$

$$h_{nb} = 800 \text{ W/m}^2\text{°C}$$

$$Re_L f_c^{1.25} = 79,040 \times 3.2^{1.25} = 338,286$$

From Figure 12.57,  $f_s = 0.13$ ,

$$h'_{nb} = 0.13 \times 800 = 104 \text{ W/m}^2\text{°C}$$

$$h_{cb} = 9824 + 104 = \underline{\underline{9928 \text{ W/m}^2\text{°C}}}$$

#### 12.11.4. Design of forced-circulation reboilers

The normal practice in the design of forced-convection reboilers is to calculate the heat-transfer coefficient assuming that the heat is transferred by forced convection only. This will give conservative (safe) values, as any boiling that occurs will invariably increase the rate of heat transfer. In many designs the pressure is controlled to prevent any appreciable vaporisation in the exchanger. A throttle valve is installed in the exchanger outlet line, and the liquid flashes as the pressure is let down into the vapour-liquid separation vessel.

If a significant amount of vaporisation does occur, the heat-transfer coefficient can be evaluated using correlations for convective boiling, such as Chen's method.

Conventional shell and tube exchanger designs are used, with one shell pass and two tube passes, when the process fluid is on the shell side; and one shell and one tube pass when it is in the tubes. High tube velocities are used to reduce fouling, 3–9 m/s.

Because the circulation rate is set by the designer, forced-circulation reboilers can be designed with more certainty than natural circulation units.

The critical flux in forced-convection boiling is difficult to predict. Kern (1950) recommends that for commercial reboiler designs the heat flux should not exceed  $63,000 \text{ W/m}^2$  ( $20,000 \text{ Btu/ft}^2\text{h}$ ) for organics and  $95,000 \text{ W/m}^2$  ( $30,000 \text{ Btu/ft}^2\text{h}$ ) for water and dilute aqueous solutions. These values are now generally considered to be too pessimistic.

### 12.11.5. Design of thermosyphon reboilers

The design of thermosyphon reboilers is complicated by the fact that, unlike a forced-convection reboiler, the fluid circulation rate cannot be determined explicitly. The circulation rate, heat-transfer rate and pressure drop are all interrelated, and iterative design procedures must be used. The fluid will circulate at a rate at which the pressure losses in the system are just balanced by the available hydrostatic head. The exchanger, column base and piping can be considered as the two legs of a U-tube; Figure 12.58. The driving force for circulation round the system is the difference in density of the liquid in the “cold” leg (the column base and inlet piping) and the two-phase fluid in the “hot” leg (the exchanger tubes and outlet piping).

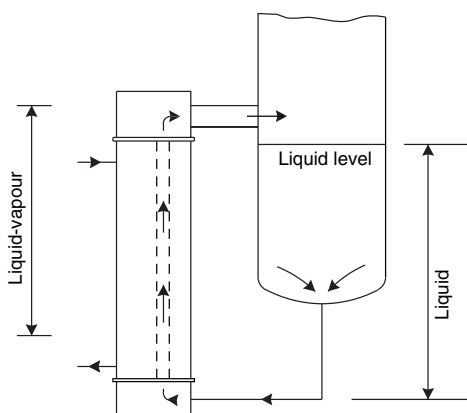


Figure 12.58. Vertical thermosyphon reboiler, liquid and vapour flows

To calculate the circulation rate it is necessary to make a pressure balance round the system.

A typical design procedure will include the following steps:

1. Calculate the vaporisation rate required; from the specified duty.
2. Estimate the exchanger area; from an assumed value for the overall heat-transfer coefficient. Decide the exchanger layout and piping dimensions.
3. Assume a value for the circulation rate through the exchanger.
4. Calculate the pressure drop in the inlet piping (single phase).
5. Divide the exchanger tube into sections and calculate the pressure drop section-by-section up the tube. Use suitable methods for the sections in which the flow is two-phase. Include the pressure loss due to the fluid acceleration as the vapour rate increases. For a horizontal reboiler, calculate the pressure drop in the shell, using a method suitable for two-phase flow.

6. Calculate the pressure drop in the outlet piping (two-phase).
7. Compare the calculated pressure drop with the available differential head; which will depend on the vapour voidage, and hence the assumed circulation rate. If a satisfactory balance has been achieved, proceed. If not, return to step 3 and repeat the calculations with a new assumed circulation rate.
8. Calculate the heat-transfer coefficient and heat-transfer rate section-by-section up the tubes. Use a suitable method for the sections in which the boiling is occurring; such as Chen's method.
9. Calculate the rate of vaporisation from the total heat-transfer rate, and compare with the value assumed in step 1. If the values are sufficiently close, proceed. If not, return to step 2 and repeat the calculations for a new design.
10. Check that the critical heat flux is not exceeded at any point up the tubes.
11. Repeat the complete procedure as necessary to optimise the design.

It can be seen that to design a thermosyphon reboiler using hand calculations would be tedious and time-consuming. The iterative nature of the procedure lends itself to solution by computers. Sarma *et al.* (1973) discuss the development of a computer program for vertical thermosyphon reboiler design, and give algorithms and design equations.

Extensive work on the performance and design of thermosyphon reboilers has been carried out by HTFS and HTRI, and proprietary design programs are available from these organisations.

In the absence of access to a computer program the rigorous design methods given by Fair (1960, 1963) or Hughmark (1961, 1964, 1969) can be used for thermosyphon vertical reboilers. Collins (1976) and Fair and Klip (1983) give methods for the design of horizontal, shell-side thermosyphon reboilers. The design and performance of this type of reboiler is also reviewed in a paper by Yilmaz (1987).

Approximate methods can be used for preliminary designs. Fair (1960) gives a method in which the heat transfer and pressure drop in the tubes are based on the average of the inlet and outlet conditions. This simplifies step 5 in the design procedure but trial-and-error calculations are still needed to determine the circulation rate. Frank and Prickett (1973) programmed Fair's rigorous design method for computer solution and used it, together with operating data on commercial exchangers, to derive a general correlation of heat-transfer rate with reduced temperature for vertical thermosyphon reboilers. Their correlation, converted to SI units, is shown in Figure 12.59. The basis and limitations of the correlation are listed below:

1. Conventional designs: tube lengths 2.5 to 3.7 m (8 to 12 ft) (standard length 2.44 m), preferred diameter 25 mm (1 in.).
2. Liquid in the sump level with the top tube sheet.
3. Process side fouling coefficient  $6000 \text{ W/m}^2\text{°C}$ .
4. Heating medium steam, coefficient including fouling,  $6000 \text{ W/m}^2\text{°C}$ .
5. Simple inlet and outlet piping.
6. For reduced temperatures greater than 0.8, use the limiting curve (that for aqueous solutions).
7. Minimum operating pressure 0.3 bar.
8. Inlet fluid should not be appreciably sub-cooled.
9. Extrapolation is not recommended.

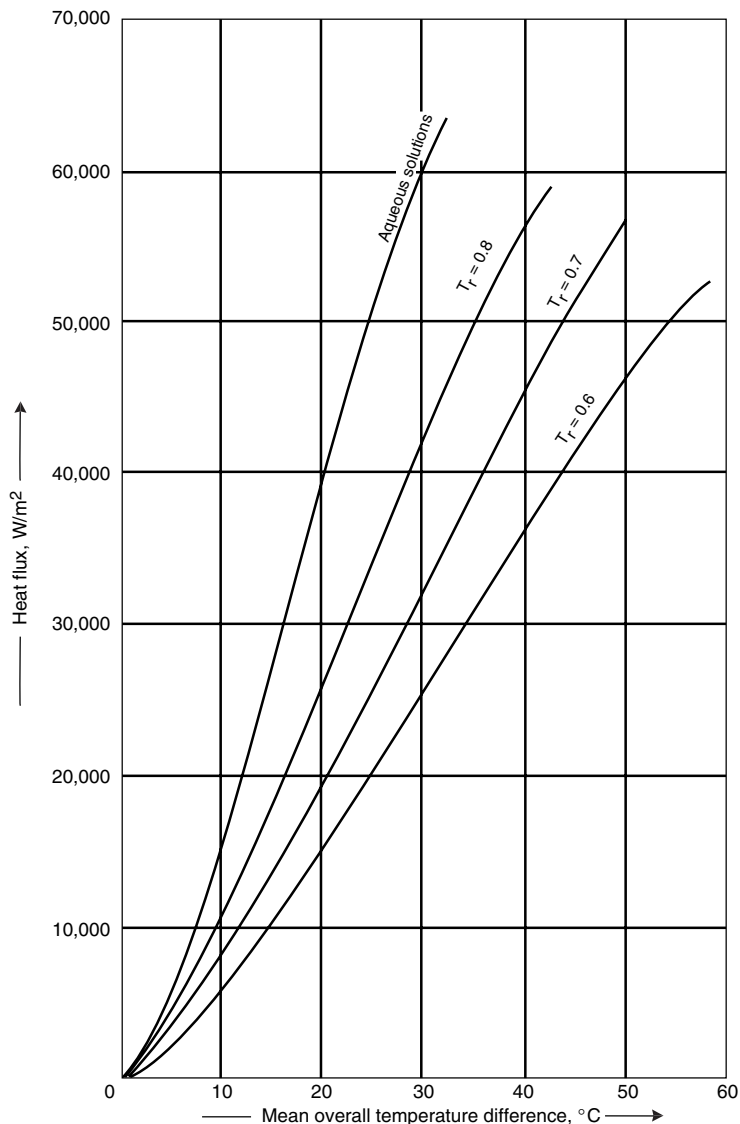


Figure 12.59. Vertical thermosyphon design correlation

For heating media other than steam and process side fouling coefficients different from  $6000 \text{ W/m}^2\text{°C}$ , the design heat flux taken from Figure 12.59 may be adjusted as follows:

$$U' = \frac{q'}{\Delta T'} \tag{12.72}$$

and

$$\frac{1}{U_c} = \frac{1}{U'} - \frac{1}{6000} + \frac{1}{h_s} - \frac{1}{6000} + \frac{1}{h_{id}}$$



where  $q'$  = flux read from Figure 12.59 at  $\Delta T'$ ,

$h_s$  = new shell side coefficient  $\text{W/m}^2\text{°C}$ ,

$h_{id}$  = fouling coefficient on the process (tube) side  $\text{W/m}^2\text{°C}$ ,

$U_c$  = corrected overall coefficient.

The use of Frank and Prickett's method is illustrated in Example 12.10.

### **Limitations on the use of Frank and Prickett's method**

A study by van Edmonds (1994), using the HTFS TREB4 program, found that Frank and Prickett's method gave acceptable predictions for pure components and binary mixtures with water, but that the results were unreliable for other mixtures. Also, van Edmonds' results predicted higher flux values than those obtained by Prickett and Frank.

For preliminary designs for pure components, or near pure components, Prickett and Frank's method should give a conservative estimate of the operating heat flux. It is not recommended for mixtures, other than binary mixtures with water.

### **Approximate design method for mixtures**

For mixtures, the simplified analysis used by Kern (1954) can be used to obtain an approximate estimate of the number of tubes required; see also Aerstin and Street (1978) and Hewitt *et al.* (1994).

This method uses simple, unsophisticated, methods to estimate the two-phase pressure drop through the exchanger and piping, and the convective boiling heat transfer coefficient. The calculation procedure is set out below and illustrated in Example 12.11

### **Procedure**

1. Determine the heat duty.
2. Estimate the heat transfer area, using the maximum allowable heat flux. Take as  $39,700 \text{ W/m}^2$  for vertical and  $47,300 \text{ W/m}^2$  for horizontal reboilers.
3. Choose the tube diameters and length. Calculate the number of tubes required.
4. Estimate the recirculation ratio, not less than 3.
5. Calculate the vapour flow rate leaving the reboiler for the duty and liquid heat of vaporisation.
6. Calculate the liquid flow rate leaving the reboiler for the vapour rate and recirculation ratio.
7. Estimate the two-phase pressure drop through the tubes, due to friction. Use the homogenous model or another simple method, such as the Lochart–Martelli equation; see Volume 1, Chapter 5.
8. Estimate the static head in the tubes.
9. Estimate the available head.
10. Compare the total estimated pressure drop and the available head. If the available head is greater by a sufficient amount to allow for the pressure drop through the inlet and outlet piping, proceed. If the available head is not sufficient, return to step 2, and increase the number of tubes.
11. Calculate the convective heat transfer coefficient using simple methods, such as assuming convection only, or Chens' method; see Section 12.11.3.

12. Calculate the overall heat transfer coefficient.
13. Calculate the required overall coefficient and compare with that estimated. If satisfactory, accept the design, if unsatisfactory return to step 2 and increase the estimated area.

### **Maximum heat flux**

Thermosyphon reboilers can suffer from flow instabilities if too high a heat flux is used. The liquid and vapour flow in the tubes is not smooth but tends to pulsate, and at high heat fluxes the pulsations can become large enough to cause vapour locking. A good practice is to install a flow restriction in the inlet line, a valve or orifice plate, so that the flow resistance can be adjusted should vapour locking occur in operation.

Kern recommends that the heat flux in thermosyphon reboilers, based on the total heat-transfer area, should not exceed  $37,900 \text{ W/m}^2$  ( $12,000 \text{ Btu/ft}^2\text{h}$ ). For horizontal thermosyphon reboilers, Collins recommends a maximum flux ranging from  $47,300 \text{ W/m}^2$  for 20-mm tubes to  $56,800 \text{ W/m}^2$  for 25-mm tubes ( $15,000$  to  $18,000 \text{ Btu/ft}^2\text{h}$ ). These “rule of thumb” values are now thought to be too conservative; see Skellence *et al.* (1968) and Furzer (1990). Correlations for determining the maximum heat flux for vertical thermosyphons are given by Lee *et al.* (1956) and Palen *et al.* (1974); and for horizontal thermosyphons by Yilmaz (1987).

### **General design considerations**

The tube lengths used for vertical thermosyphon reboilers vary from 1.83 m (6 ft) for vacuum service to 3.66 m (12 ft) for pressure operation. A good size for general applications is 2.44 m (8 ft) by 25 mm internal diameter. Larger tube diameters, up to 50 mm, are used for fouling systems.

The top tube sheet is normally aligned with the liquid level in the base of the column; Figure 12.58. The outlet pipe should be as short as possible, and have a cross-sectional area at least equal to the total cross-sectional area of the tubes.

### **Example 12.10**

Make a preliminary design for a vertical thermosyphon for a column distilling crude aniline. The column will operate at atmospheric pressure and a vaporisation rate of 6000 kg/h is required. Steam is available at 22 bar (300 psig). Take the column bottom pressure as 1.2 bar.

### **Solution**

Physical properties, taken as those of aniline:

Boiling point at 1.2 bar  $190^\circ\text{C}$

Molecular weight 93.13

$T_c$  699 K

Latent heat 42,000 kJ/kmol

Steam saturation temperature  $217^\circ\text{C}$ .

Mean overall  $\Delta T = (217 - 190) = 27^\circ\text{C}$ .

$$\text{Reduced temperature, } T_r = \frac{(190 + 273)}{699} = 0.66$$

From Figure 12.59, design heat flux = 25,000 W/m<sup>2</sup>

$$\text{Heat load} = \frac{6000}{3600} \times \frac{42,000}{93.13} = 751 \text{ kW}$$

$$\text{Area required} = \frac{751 \times 10^3}{25,000} = 30 \text{ m}^2$$

Use 25 mm i.d., 30 mm o.d., 2.44 m long tubes.

$$\text{Area of one tube} = \pi 25 \times 10^{-3} \times 2.44 = 0.192 \text{ m}^2$$

$$\text{Number of tubes} = \frac{30}{0.192} = 157$$

Approximate diameter of bundle, for 1.25 square pitch

$$D_b = 30 \left[ \frac{157}{0.215} \right]^{1/2.207} = 595 \text{ mm} \quad (12.3b)$$

A fixed tube sheet will be used for a vertical thermosyphon reboiler. From Figure 12.10, shell diametrical clearance = 14 mm,

$$\text{Shell inside dia.} = 595 + 14 = 609 \text{ mm}$$

Outlet pipe diameter; take area as equal to total tube cross-sectional area

$$= 157(25 \times 10^{-3})^2 \frac{\pi}{4} = 0.077 \text{ m}^2$$

$$\text{Pipe diameter} = \sqrt{\frac{0.077 \times 4}{\pi}} = 0.31 \text{ m}$$

### Example 12.11

Make a preliminary design for a vertical thermosyphon reboiler for the column specified in Example 11.9. Take the vapour rate required to be 36 kmol/h.

From example 8.3:

Operating pressure 8.3 (neglecting pressure drop over column).

Bottoms composition: C<sub>3</sub> 0.001, iC<sub>4</sub> 0.001, nC<sub>4</sub> 0.02, iC<sub>5</sub> 0.34, nC<sub>5</sub> 0.64, kmol.

Bubble point of mixture, approximately, 120°C.

### Solution

The concentrations of C<sub>3</sub> and iC<sub>4</sub> are small enough to be neglected.

Take the liquid: vapour ratio as 3 : 1.

Estimate the liquid and vapour compositions leaving the reboiler:

Vapour rate,  $V = 36/3600 = 0.1$  kmol/s

$L/V = 3$ , so liquid rate,  $L = 3 V = 0.3$  kmol/s and feed,  $F = L + V = 0.4$  kmol/s.

The vapour and liquid compositions leaving the reboiler can be estimated using the same procedure as that for a flash calculation; see Section 11.3.3.

	$K_i$	$A_i = K_i \times L/V$	$V_i = z_i/(1 + A_i)$	$y_i = V_i/V$	$x_i = (Fz_i - V_i)/L$
nC <sub>4</sub>	2.03	6.09	0.001	0.010	0.023
iC <sub>5</sub>	1.06	3.18	0.033	0.324	0.343
nC <sub>5</sub>	0.92	2.76	0.068	0.667	0.627
Totals			0.102	1.001	0.993

(near enough correct)

Enthalpies of vaporisation, from Figures (b) and (c) Example 11.9, kJ/mol

	$x_i$	$H_i$	$h_i$	$H_i - h_i$	$x_i(H_i - h_i)$
nC <sub>4</sub>	0.02	50	34	16	0.32
iC <sub>5</sub>	0.35	58	41	17	5.95
nC <sub>5</sub>	0.63	61	42	19	11.97
Total					18.24

Exchanger duty, feed to reboiler taken as at its boiling point

= vapour flow-rate  $\times$  heat of vaporisation

$$= 0.1 \times 10^3 \times 18.24 = \underline{\underline{1824}} \text{ kW}$$

Take the maximum flux as 37,900 W/m<sup>2</sup>; see Section 12.11.5.

Heat transfer area required = 1,824,000/37,900 = 48.1 m<sup>2</sup>

Use 25 mm i.d., 2.5 m long tubes, a popular size for vertical thermosyphon reboilers.

Area of one tube =  $25 \times 10^{-3} \pi \times 2.5 = 0.196$  m<sup>2</sup>

Number of tubes required = 48.1/0.196 = 246

Liquid density at base of exchanger = 520 kg/m<sup>3</sup>

Relative molecular mass at tube entry =  $58 \times 0.02 + 72(0.34 + 0.64) = 71.7$

vapour at exit =  $58 \times 0.02 + 72(0.35 + 0.63) = 71.7$

Two-phase fluid density at tube exit:

volume of vapour =  $0.1 \times (22.4/8.3) \times (393/273) = 0.389$  m<sup>3</sup>

volume of liquid =  $(0.3 \times 71.7)/520 = 0.0413$  m<sup>3</sup>

total volume = 0.389 + 0.0413 = 0.430 m<sup>3</sup>

exit density =  $\frac{(0.4 \times 71.7)}{0.430} \times 71.7 = 66.7$  kg/m<sup>3</sup>

### Friction loss

Mass flow-rate =  $0.4 \times 71.7 = 28.68$  kg/s

Cross-sectional area of tube =  $\frac{\pi(25 \times 10^{-3})^2}{4} = 0.00049$  m<sup>2</sup>

Total cross-sectional area of bundle =  $246 \times 0.00049 = 0.121 \text{ m}^2$

Mass flux,  $G = \text{mass flow/area} = 28.68/0.121 = 237.0 \text{ kg m}^{-2} \text{ s}^{-1}$

At tube exit, pressure drop per unit lengths, using the homogeneous model:

homogeneous velocity =  $G/\rho_m = 237/66.7 = 3.55 \text{ m/s}$

Viscosity, taken as that of liquid, =  $0.12 \text{ mN sm}^{-2}$

$$Re = \frac{\rho_m u d}{\mu} = \frac{66.7 \times 3.55 \times 25 \times 10^{-3}}{0.12 \times 10^{-3}} = 49,330, (4.9 \times 10^4)$$

Friction factor, from Fig. 12.24 =  $3.2 \times 10^{-3}$

$$\Delta P_f = 8 \times 3.2 \times 10^{-3} \times \frac{1}{25 \times 10^{-3}} \times 66.7 \times \frac{3.55^2}{2} = 430 \text{ N/m}^2 \text{ per m} \quad (12.19)$$

At tube entry, liquid only, pressure drop per unit length:

velocity =  $G/\rho_L = 237.0/520 = 0.46 \text{ m/s}$

$$Re = \frac{\rho_L u d}{\mu} = \frac{520 \times 0.46 \times 25 \times 10^{-3}}{0.12 \times 10^{-3}} = 49,833, (5.0 \times 10^4)$$

Friction factor, from Fig 12.24 =  $3.2 \times 10^{-3}$

$$\Delta P_f = 8 \times 3.2 \times 10^{-3} \times \frac{1}{25 \times 10^{-3}} \times 520 \times \frac{0.46^2}{2} = 56 \text{ N/m}^2 \text{ per m} \quad (12.19)$$

Taking the pressure drop change as linear along the tube,

Mean pressure drop per unit length =  $(430 + 56)/2 = 243 \text{ N/m}^2$

Pressure drop over tube  $243 \times 2.5 = 608 \text{ N/m}^2$

The viscosity correction factor is neglected in this rough calculation.

### *Static pressure in tubes*

Making the simplifying assumption that the variation in density in the tubes is linear from bottom to top, the static pressure will be given by:

$$\Delta P_s = g \int_0^L \frac{dx}{v_i + x(v_0 - v_i)/L} = \frac{gL}{(v_0 - v_i)} \times \text{Ln}(v_0/v_i)$$

where  $v_i$  and  $v_0$  are the inlet and outlet specific volumes.

$v_i = 1/520 = 0.00192$  and  $v_0 = 1/66.7 = 0.0150 \text{ m}^3/\text{kg}$

$$\Delta P_s = \frac{9.8 \times 2.5}{(0.0150 - 0.00192)} \times \text{Ln}(0.0150/0.00192) = 3850 \text{ N/m}^2$$

Total pressure drop over tubes =  $346 + 3850 = \underline{\underline{4250}} \text{ N/m}^2$

### *Available head (driving force)*

$$\Delta P_a = \rho_L g L = 520 \times 9.8 \times 2.5 = \underline{\underline{12,740}} \text{ N/m}^2$$

Which is adequate to maintain a circulation ratio of 3 : 1, including allowances for the pressure drop across the piping.

### Heat transfer

The convective boiling coefficient will be calculated using Chen's method; see Section 12.13.3.

As the heat flux is known and only a rough estimate of the coefficient is required, use Mostinski's equation to estimate the nucleate boiling coefficient; Section 12.11.2.

Take the critical pressure as that for n-pentane, 33.7 bar.

$$\begin{aligned} h_{nb} &= 0.104(33.7)^{0.69}(37,900)^{0.7}[1.8(8.3/33.7)^{0.17} \\ &\quad + 4(8.3/33.7)^{1.2} + 10(8.3/33.7)^{10}] \\ &= 1888.6(1.418 + 0.744 + 0.000) = 4083 \text{ Wm}^{-2}\text{C}^{-1} \end{aligned} \quad (12.63)$$

Vapour quality,  $x = \text{mass vapour}/\text{total mass flow} = 0.1/0.4 = 0.25$

Viscosity of vapour =  $0.0084 \text{ mNm}^{-2}\text{s}$

Vapour density at tube exit =  $(0.1 \times 71.7)/0.389 = 18.43 \text{ kg/m}^3$

$$1/X_{tt} = [0.25/(1 - 0.25)]^{0.9}[520/18.43]^{0.5}[0.0084/0.12]^{0.1} = 1.51 \quad (12.69)$$

Specific heat of liquid =  $2.78 \text{ kJkg}^{-1}\text{C}^{-1}$ , thermal conductivity of liquid =  $0.12 \text{ Wm}^{-1}\text{C}^{-1}$ .

$$Pr_L = (2.78 \times 10^3 \times 0.12 \times 10^{-3})/0.12 = 2.78$$

Mass flux, liquid phase only flowing in tubes =  $(0.3 \times 71.7)/0.121 = 177.8 \text{ kg m}^{-2}\text{s}^{-1}$

Velocity =  $177.8/520 = 0.34 \text{ m/s}$

$$Re_L = \frac{520 \times 0.34 \times 25 \times 10^{-3}}{0.12 \times 10^{-3}} = 36,833 \quad (3.7 \times 10^4)$$

From Figure 12.23  $j_h = 3.3 \times 10^{-3}$ ,

$$Nu = 3.3 \times 10^{-3} \times 36,833 \times 2.78^{0.33} = 170.3 \quad (12.15)$$

$$h_i = 170.3 \times (0.12/25 \times 10^{-3}) = 817 \text{ Wm}^{-2}\text{C}^{-1}$$

again, neglecting the viscosity correction factor.

From Figure 12.56, the convective boiling factor,  $f_c = 3.6$

$$Re_L \times f_c^{1.25} = 36,833 \times 3.6^{1.25} = 182,896 \quad (1.8 \times 10^5)$$

From Figure 12.57 the nucleate boiling suppression factor,  $f_s = 0.23$

$$\text{So, } h_{cb} = 3.6 \times 817 + 0.23 \times 4083 = 3880 \text{ Wm}^{-2}\text{C}^{-1}$$

This value has been calculated at the outlet conditions.

Assuming that the coefficient changes linearly for the inlet to outlet, then the average coefficient will be given by:

$$[\text{inlet coefficient (all liquid)} + \text{outlet coefficient (liquid + vapour)}]/2$$

$$Re_L \text{ at inlet} = 36,833 \times 0.4/0.3 = 49,111 \quad (4.9 \times 10^{-4})$$

$$\text{From Figure 12.23, } j_h = 3.2 \times 10^{-3}$$

$$Nu = 3.2 \times 10^{-3} \times 49,111 \times 2.78^{0.33} = 220.2 \quad (12.15)$$

$$h_i = 220.2 \times (0.12/25 \times 10^{-3}) = 1057 \text{ Wm}^{-2}\text{C}^{-1}$$

$$\text{Mean coefficient} = (1057 + 3880)/2 = \underline{2467} \text{ Wm}^{-2}\text{C}^{-1}$$

The overall coefficient,  $U$ , neglecting the resistance of the tube wall, and taking the steam coefficient as  $8000 \text{ Wm}^{-2}\text{C}^{-1}$ , is given by:

$$1/U = 1/8000 + 1/2467 = 5.30 \times 10^{-4}$$

$$U = \underline{1886} \text{ Wm}^{-2}\text{C}^{-1}$$

The overall coefficient required for the design = duty/ $\Delta T_{LM}$

$$\Delta T_{LM} = 158.8 - 120 = 38.8^\circ\text{C}, \text{ taking both streams as isothermal}$$

$$\text{So, } U \text{ required} = 37,900/38.3 = \underline{990} \text{ Wm}^{-2}\text{C}^{-1}$$

So the area available in the proposed design is more than adequate and will take care of any fouling.

The analysis could be improved by dividing the tube length into sections, calculating the heat transfer coefficient and pressure drop over each section, and totalling.

More accurate, but more complex, methods could be used to predict the two-phase pressure drop and heat transfer coefficients.

The pressure drop over the inlet and outlet pipes could also be estimated, taking into account the bends, and expansions and contractions.

An allowance could also be included for the energy (pressure drop) required to accelerate the liquid–vapour mixtures as the liquid is vaporised. This can be taken as two velocity head, based on the mean density.

### 12.11.6. Design of kettle reboilers

Kettle reboilers, and other submerged bundle equipment, are essentially pool boiling devices, and their design is based on data for nucleate boiling.

In a tube bundle the vapour rising from the lower rows of tubes passes over the upper rows. This has two opposing effects: there will be a tendency for the rising vapour to blanket the upper tubes, particularly if the tube spacing is close, which will reduce the heat-transfer rate; but this is offset by the increased turbulence caused by the rising vapour bubbles. Palen and Small (1964) give a detailed procedure for kettle reboiler design in

which the heat-transfer coefficient calculated using equations for boiling on a single tube is reduced by an empirically derived tube bundle factor, to account for the effects of vapour blanketing. Later work by Heat Transfer Research Inc., reported by Palen *et al.* (1972), showed that the coefficient for bundles was usually greater than that estimated for a single tube. On balance, it seems reasonable to use the correlations for single tubes to estimate the coefficient for tube bundles without applying any correction (equations 12.62 or 12.63).

The maximum heat flux for stable nucleate boiling will, however, be less for a tube bundle than for a single tube. Palen and Small (1964) suggest modifying the Zuber equation for single tubes (equation 12.64) with a tube density factor. This approach was supported by Palen *et al.* (1972).

The modified Zuber equation can be written as:

$$q_{cb} = K_b \left( \frac{p_t}{d_o} \right) \left( \frac{\lambda}{\sqrt{N_t}} \right) [\sigma g(\rho_L - \rho_v)\rho_v^2]^{0.25} \quad (12.74)$$

where  $q_{cb}$  = maximum (critical) heat flux for the tube bundle, W/m<sup>2</sup>,

$K_b$  = 0.44 for square pitch arrangements,

= 0.41 for equilateral triangular pitch arrangements,

$p_t$  = tube pitch,

$d_o$  = tube outside diameter,

$N_t$  = total number of tubes in the bundle,

*Note.* For U-tubes  $N_t$  will be equal to twice the number of actual U-tubes.

Palen and Small suggest that a factor of safety of 0.7 be applied to the maximum flux estimated from equation 12.74. This will still give values that are well above those which have traditionally been used for the design of commercial kettle reboilers; such as that of 37,900 W/m<sup>2</sup> (12,000 Btu/ft<sup>2</sup>h) recommended by Kern (1950). This has had important implications in the application of submerged bundle reboilers, as the high heat flux allows a smaller bundle to be used, which can then often be installed in the base of the column; saving the cost of shell and piping.

### General design considerations

A typical layout is shown in Figure 12.8. The tube arrangement, triangular or square pitch, will not have a significant effect on the heat-transfer coefficient. A tube pitch of between 1.5 to 2.0 times the tube outside diameter should be used to avoid vapour blanketing. Long thin bundles will be more efficient than short fat bundles.

The shell should be sized to give adequate space for the disengagement of the vapour and liquid. The shell diameter required will depend on the heat flux. The following values can be used as a guide:

Heat flux W/m <sup>2</sup>	Shell dia./Bundle dia.
25,000	1.2 to 1.5
25,000 to 40,000	1.4 to 1.8
40,000	1.7 to 2.0



The freeboard between the liquid level and shell should be at least 0.25 m. To avoid excessive entrainment, the maximum vapour velocity  $\hat{u}_v$  (m/s) at the liquid surface should be less than that given by the expression:

$$\hat{u}_v < 0.2 \left[ \frac{\rho_L - \rho_v}{\rho_v} \right]^{1/2} \quad (12.75)$$

When only a low rate of vaporisation is required a vertical cylindrical vessel with a heating jacket or coils should be considered. The boiling coefficients for internal submerged coils can be estimated using the equations for nucleate pool boiling.

### **Mean temperature differences**

When the fluid being vaporised is a single component and the heating medium is steam (or another condensing vapour), both shell and tubes side processes will be isothermal and the mean temperature difference will be simply the difference between the saturation temperatures. If one side is not isothermal the logarithmic mean temperature difference should be used. If the temperature varies on both sides, the logarithmic temperature difference must be corrected for departures from true cross- or counter-current flow (see Section 12.6).

If the feed is sub-cooled, the mean temperature difference should still be based on the boiling point of the liquid, as the feed will rapidly mix with the boiling pool of liquid; the quantity of heat required to bring the feed to its boiling point must be included in the total duty.

### **Mixtures**

The equations for estimating nucleate boiling coefficients given in Section 12.11.1 can be used for close boiling mixtures, say less than 5°C, but will overestimate the coefficient if used for mixtures with a wide boiling range. Palen and Small (1964) give an empirical correction factor for mixtures which can be used to estimate the heat-transfer coefficient in the absence of experimental data:

$$(h_{nb}) \text{ mixture} = f_m (h_{nb}) \text{ single component} \quad (12.76)$$

where  $f_m = \exp[-0.0083(T_{bo} - T_{bi})]$

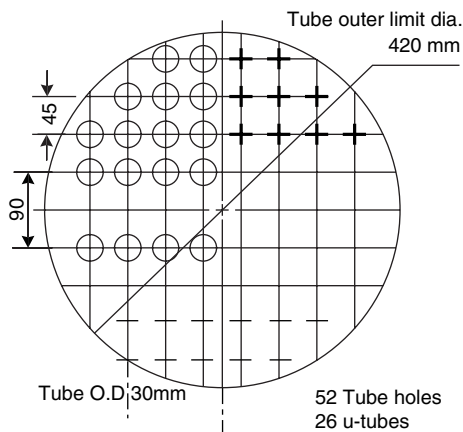
and  $T_{bo}$  = temperature of the vapour mixture leaving the reboiler °C,

$T_{bi}$  = temperature of the liquid entering the reboiler °C.

The inlet temperature will be the saturation temperature of the liquid at the base of the column, and the vapour temperature the saturation temperature of the vapour returned to the column. The composition of these streams will be fixed by the distillation column design specification.

### **Example 12.12**

Design a vaporiser to vaporise 5000 kg/h n-butane at 5.84 bar. The minimum temperature of the feed (winter conditions) will be 0°C. Steam is available at 1.70 bar (10 psig).



Tube sheet layout, U-tubes, Example 12.9

### Solution

Only the thermal design and general layout will be done. Select kettle type.

Physical properties of n-butane at 5.84 bar:

boiling point = 56.1°C

latent heat = 326 kJ/kg

mean specific heat, liquid = 2.51 kJ/kg°C

critical pressure,  $P_c = 38$  bar

Heat loads:

$$\text{sensible heat (maximum)} = (56.1 - 0)2.51 = 140.8 \text{ kJ/kg}$$

$$\text{total heat load} = (140.8 + 326) \times \frac{5000}{3600} = 648.3 \text{ kW,}$$

add 5 per cent for heat losses

$$\begin{aligned} \text{maximum heat load (duty)} &= 1.05 \times 648.3 \\ &= 681 \text{ kW} \end{aligned}$$

From Figure 12.1 assume  $U = 1000 \text{ W/m}^2\text{°C}$ .

Mean temperature difference; both sides isothermal, steam saturation temperature at 1.7 bar = 115.2°C

$$\Delta T_m = 115.2 - 56.1 = 59.1^\circ\text{C}$$

$$\text{Area (outside) required} = \frac{681 \times 10^3}{1000 \times 59.1} = 11.5 \text{ m}^2$$

Select 25 mm i.d., 30 mm o.d. plain U-tubes,

Nominal length 4.8 m (one U-tube)

$$\text{Number of U tubes} = \frac{11.5}{(30 \times 10^{-3})\pi 4.8} = 25$$

Use square pitch arrangement, pitch =  $1.5 \times$  tube o.d.  
 $= 1.5 \times 30 = 45$  mm

Draw a tube layout diagram, take minimum bend radius

$$1.5 \times \text{tube o.d.} = 45 \text{ mm}$$

Proposed layout gives 26 U-tubes, tube outer limit diameter 420 mm.

Boiling coefficient

Use Mostinski's equation:

heat flux, based on estimated area,

$$q = \frac{681}{11.5} = 59.2 \text{ kW/m}^2$$

$$h_{nb} = 0.104(38)^{0.69}(59.2 \times 10^3)^{0.7} \left[ 1.8 \left( \frac{5.84}{38} \right)^{0.17} + 4 \left( \frac{5.84}{38} \right)^{1.2} + 10 \left( \frac{5.84}{38} \right)^{10} \right]$$

$$= 4855 \text{ W/m}^2\text{°C} \quad (12.63)$$

Take steam condensing coefficient as  $8000 \text{ W/m}^2\text{°C}$ , fouling coefficient  $5000 \text{ W/m}^2\text{°C}$ ; butane fouling coefficient, essentially clean,  $10,000 \text{ W/m}^2\text{°C}$ .

Tube material will be plain carbon steel,  $k_w = 55 \text{ W/m}^2\text{°C}$

$$\frac{1}{U_o} = \frac{1}{4855} + \frac{1}{10,000} + \frac{30 \times 10^{-3} \ln \frac{30}{25}}{2 \times 55} + \frac{30}{25} \left( \frac{1}{5000} + \frac{1}{8000} \right) \quad (12.2)$$

$$U_o = \underline{\underline{1341 \text{ W/m}^2\text{°C}}}$$

Close enough to original estimate of  $1000 \text{ W/m}^2\text{°C}$  for the design to stand.

Myers and Katz (*Chem. Eng. Prog. Sym. Ser.* **49**(5) 107-114) give some data on the boiling of n-butane on banks of tubes. To compare the value estimate with their values an estimate of the boiling film temperature difference is required:

$$= \frac{1341}{4855} \times 59.1 = 16.3^\circ\text{C} \text{ (29}^\circ\text{F)}$$

Myers data, extrapolated, gives a coefficient of around  $3000 \text{ Btu/h ft}^2\text{°F}$  at a  $29^\circ\text{F}$  temperature difference =  $17,100 \text{ W/m}^2\text{°C}$ , so the estimated value of 4855 is certainly on the safe side.

Check maximum allowable heat flux. Use modified Zuber equation.

Surface tension (estimated) =  $9.7 \times 10^{-3} \text{ N/m}$

$$\rho_L = 550 \text{ kg/m}^3$$

$$\rho_v = \frac{58}{22.4} \times \frac{273}{(273 + 56)} \times 5.84 = 12.6 \text{ kg/m}^3$$

$$N_t = 52$$

For square arrangement  $K_b = 0.44$

$$\begin{aligned}
 q_c &= 0.44 \times 1.5 \times \frac{326 \times 10^3}{\sqrt{52}} [9.7 \times 10^{-3} \times 9.81(550 - 12.6)12.6^2]^{0.25} \quad (12.74) \\
 &= 283,224 \text{ W/m}^2 \\
 &= 280 \text{ kW/m}^2
 \end{aligned}$$

Applying a factor of 0.7, maximum flux should not exceed  $280 \times 0.7 = 196 \text{ kW/m}^2$ . Actual flux of  $59.2 \text{ kW/m}^2$  is well below maximum allowable.

### Layout

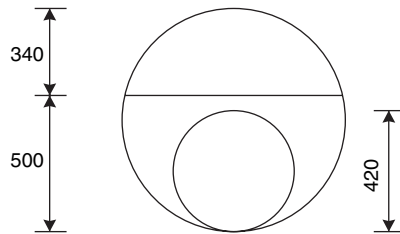
From tube sheet layout  $D_b = 420 \text{ mm}$ .

Take shell diameter as twice bundle diameter

$$D_s = 2 \times 420 = 840 \text{ mm}.$$

Take liquid level as 500 mm from base,

$$\text{freeboard} = 840 - 500 = 340 \text{ mm, satisfactory.}$$



From sketch, width at liquid level = 0.8 m.

Surface area of liquid =  $0.8 \times 2.4 = 1.9 \text{ m}^2$ .

$$\text{Vapour velocity at surface} = \frac{5000}{3600} \times \frac{1}{12.6} \times \frac{1}{1.9} = \underline{\underline{0.06 \text{ m/s}}}$$

Maximum allowable velocity

$$\hat{u}_v = 0.2 \left[ \frac{550 - 12.6}{12.6} \right]^{1/2} = \underline{\underline{1.3 \text{ m/s}}} \quad (12.75)$$

so actual velocity is well below maximum allowable velocity. A smaller shell diameter could be considered.

## 12.12. PLATE HEAT EXCHANGERS

### 12.12.1. Gasketed plate heat exchangers

A gasketed plate heat exchanger consists of a stack of closely spaced thin plates clamped together in a frame. A thin gasket seals the plates round their edges. The plates are normally between 0.5 and 3 mm thick and the gap between them 1.5 to 5 mm. Plate surface areas range from 0.03 to 1.5 m<sup>2</sup>, with a plate width:length ratio from 2.0 to 3.0. The size of plate heat exchangers can vary from very small, 0.03 m<sup>2</sup>, to very large, 1500 m<sup>2</sup>. The maximum flow-rate of fluid is limited to around 2500 m<sup>3</sup>/h.

The basic layout and flow arrangement for a gasketed plate heat exchanger is shown in Figure 12.60. Corner ports in the plates direct the flow from plate to plate. The plates are embossed with a pattern of ridges, which increase the rigidity of the plate and improve the heat transfer performance.

Plates are available in a wide range of metals and alloys; including stainless steel, aluminium and titanium. A variety of gasket materials is also used; see Table 12.8.

#### *Selection*

The advantages and disadvantages of plate heat exchangers, compared with conventional shell and tube exchangers are listed below:

#### *Advantages*

1. Plates are attractive when material costs are high.
2. Plate heat exchangers are easier to maintain.

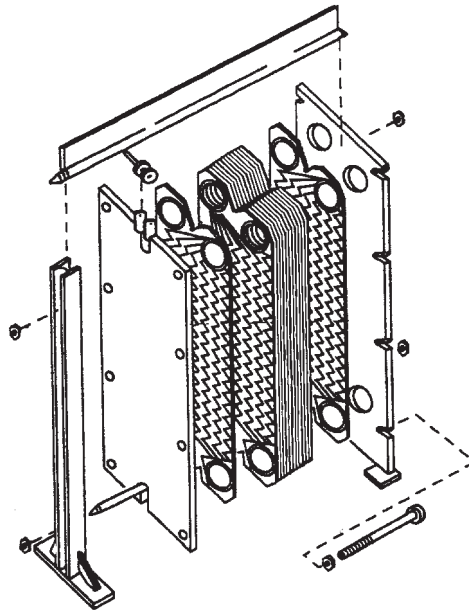


Figure 12.60. Gasketed plate heat exchanger

Table 12.8. Typical gasket materials for plated heat exchangers

Material	Approximate temperature limit, °C	Fluids
Styrene-butane rubber	85	Aqueous systems
Acrylonitrile-butane rubber	140	Aqueous system, fats, aliphatic hydrocarbons
Ethylene-propylene rubber	150	Wide range of chemicals
Fluorocarbon rubber	175	Oils
Compressed asbestos	250	General resistance to organic chemicals

3. Low approach temps can be used, as low as 1 °C, compared with 5 to 10 °C for shell and tube exchangers.
4. Plate heat exchangers are more flexible, it is easy to add extra plates.
5. Plate heat exchangers are more suitable for highly viscous materials.
6. The temperature correction factor,  $F_t$ , will normally be higher with plate heat exchangers, as the flow is closer to true counter-current flow.
7. Fouling tends to be significantly less in plate heat exchangers; see Table 12.9.

### Disadvantages

1. A plate is not a good shape to resist pressure and plate heat exchangers are not suitable for pressures greater than about 30 bar.
2. The selection of a suitable gasket is critical; see Table 12.8.
3. The maximum operating temperature is limited to about 250 °C, due to the performance of the available gasket materials.

Plate heat exchangers are used extensively in the food and beverage industries, as they can be readily taken apart for cleaning and inspection. Their use in the chemical industry will depend on the relative cost for the particular application compared with a conventional shell and tube exchanger; see Parker (1964) and Trom (1990).

Table 12.9. Fouling factors (coefficients), typical values for plate heat exchangers

Fluid	Coefficient (W/m <sup>2</sup> °C)	Factor (m <sup>2</sup> °C/W)
Process water	30,000	0.00003
Towns water (soft)	15,000	0.00007
Towns water (hard)	6000	0.00017
Cooling water (treated)	8000	0.00012
Sea water	6000	0.00017
Lubricating oil	6000	0.00017
Light organics	10,000	0.0001
Process fluids	5000–20,000	0.0002–0.00005

### Plate heat exchanger design

It is not possible to give exact design methods for plate heat exchangers. They are proprietary designs, and will normally be specified in consultation with the manufacturers. Information on the performance of the various patterns of plate used is not generally

available. Emerson (1967) gives performance data for some proprietary designs, and Kumar (1984) and Bond (1980) have published design data for APV chevron patterned plates.

The approximate method given below can be used to size an exchanger for comparison with a shell and tube exchanger, and to check performance of an existing exchanger for new duties. More detailed design methods are given by Hewitt *et al.* (1994) and Cooper and Usher (1983).

### *Procedure*

The design procedure is similar to that for shell and tube exchangers.

1. Calculate duty, the rate of heat transfer required.
2. If the specification is incomplete, determine the unknown fluid temperature or fluid flow-rate from a heat balance.
3. Calculate the log mean temperature difference,  $\Delta T_{LM}$ .
4. Determine the log mean temperature correction factor,  $F_t$ ; see method given below.
5. Calculate the corrected mean temperature difference  $\Delta T_m = F_t \times \Delta T_{LM}$ .
6. Estimate the overall heat transfer coefficient; see Table 12.1.
7. Calculate the surface area required; equation 12.1.
8. Determine the number of plates required = total surface area/area of one plate.
9. Decide the flow arrangement and number of passes.
10. Calculate the film heat transfer coefficients for each stream; see method given below.
11. Calculate the overall coefficient, allowing for fouling factors.
12. Compare the calculated with the assumed overall coefficient. If satisfactory, say  $-0\%$  to  $+10\%$  error, proceed. If unsatisfactory return to step 8 and increase or decrease the number of plates.
13. Check the pressure drop for each stream; see method given below.

This design procedure is illustrated in Example 12.13.

### **Flow arrangements**

The stream flows can be arranged in series or parallel, or a combination of series and parallel, see Figure 12.61. Each stream can be sub-divided into a number of passes; analogous to the passes used in shell and tube exchangers.

### **Estimation of the temperature correction factor**

For plate heat exchangers it is convenient to express the log mean temperature difference correction factor,  $F_t$ , as a function of the number of transfer units,  $NTU$ , and the flow arrangement (number of passes); see Figure 12.62. The correction will normally be higher for a plate heat exchanger than for a shell and tube exchanger operating with the same temperatures. For rough sizing purposes, the factor can be taken as 0.95 for series flow.

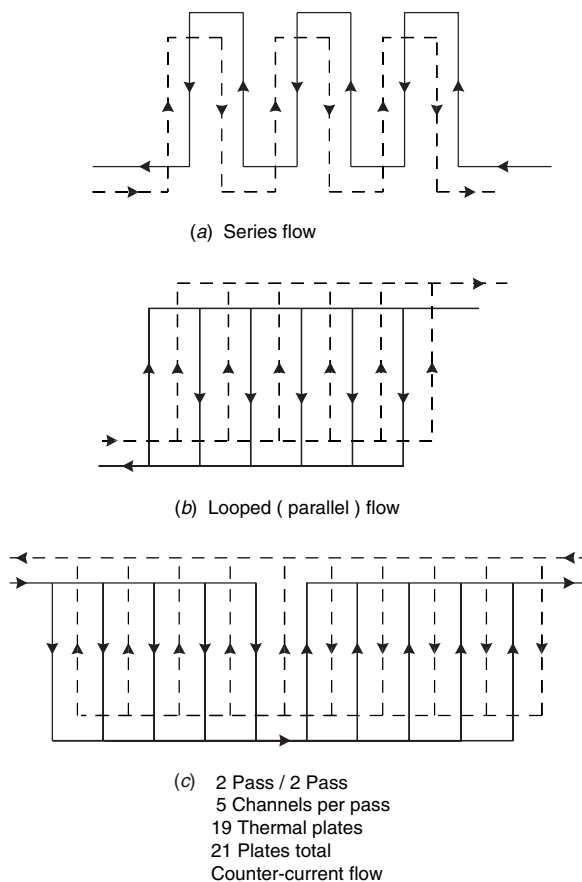


Figure 12.61. Plate heat-exchanger flow arrangements

The number of transfer units is given by:

$$NTU = (t_0 - t_i) / \Delta T_{LM}$$

where  $t_i$  = stream inlet temperature, °C,

$t_0$  = stream outlet temperature, °C,

$\Delta T_{LM}$  = log mean temperature difference, °C.

Typically, the  $NTU$  will range from 0.5 to 4.0, and for most applications will lie between 2.0 to 3.0.

### Heat transfer coefficient

The equation for forced-convective heat transfer in conduits can be used for plate heat exchangers; equation 12.10.

The values for the constant  $C$  and the indices  $a, b, c$  will depend on the particular type of plate being used. Typical values for turbulent flow are given in the equation below,



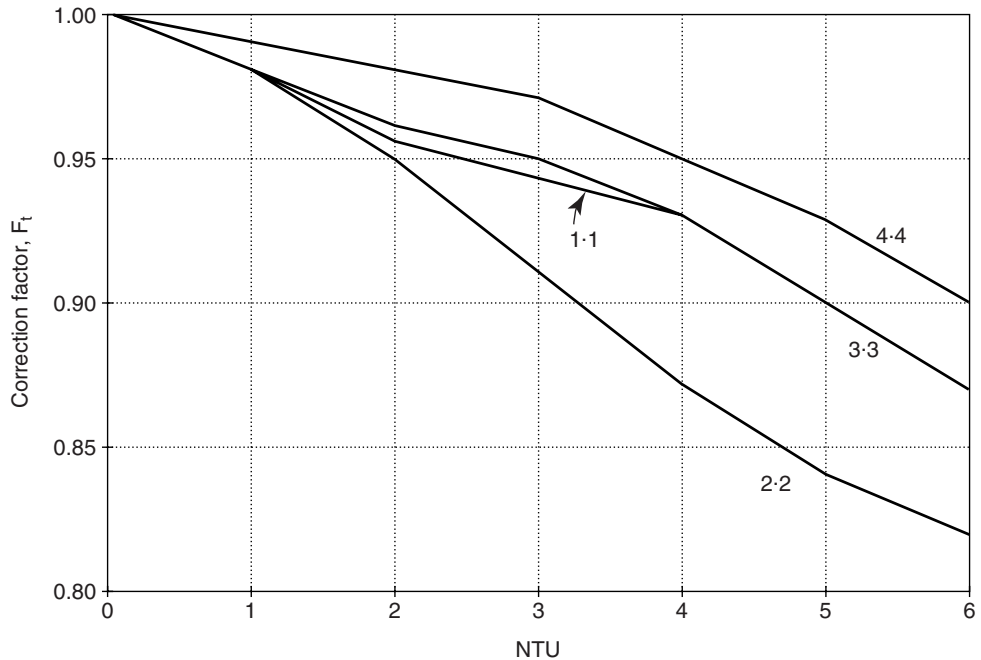


Figure 12.62. Log mean temperature correction factor for plate heat exchangers (adapted from Raju and Chand (1980))

which can be used to make a preliminary estimate of the area required.

$$\frac{h_p d_e}{k_f} = 0.26 Re^{0.65} Pr^{0.4} (\mu/\mu_w)^{0.14} \quad (12.77)$$

where  $h_p$  = plate film coefficient,

$$Re = \text{Reynold number} = \frac{G_p d_e}{\mu} = \frac{\rho u_p d_e}{\mu}$$

$G_p$  = mass flow rate per unit cross-sectional area =  $w/A_f$ ,  $\text{kgm}^{-2}\text{s}^{-1}$ ,

$w$  = mass flow rate per channel,  $\text{kg/s}$ ,

$A_f$  = cross-sectional area for flow,  $\text{m}^2$ ,

$u_p$  = channel velocity,  $\text{m/s}$ ,

$d_e$  = equivalent (hydraulic) diameter, taken as twice the gap between the plates,  $\text{m}$ .

The corrugations on the plates will increase the projected plate area, and reduce the effective gap between the plates. For rough sizing, where the actual plate design is not known, this increase can be neglected. The channel width equals the plate pitch minus the plate thickness.

There is no heat transfer across the end plates, so the number of effective plates will be the total number of plates less two.

### Pressure drop

The plate pressure drop can be estimated using a form of the equation for flow in a conduit; equation 12.18.

$$\Delta P_p = 8j_f(L_p/d_e)\frac{\rho u_p^2}{2} \quad (12.78)$$

where  $L_p$  = the path length and  $u_p = G_p/\rho$ .

The value of the friction factor,  $j_f$ , will depend on the design of plate used. For preliminary calculations the following relationship can be used for turbulent flow:

$$j_f = 0.6 Re^{-0.3}$$

The transition from laminar to turbulent flow will normally occur at a Reynolds number of 100 to 400, depending on the plate design. With some designs, turbulence can be achieved at very low Reynolds numbers, which makes plate heat exchangers very suitable for use with viscous fluids.

The pressure drop due the contraction and expansion losses through the ports in the plates must be added to the friction loss. Kumar (1984) suggests adding 1.3 velocity heads per pass, based on the velocity through the ports.

$$\Delta P_{pt} = 1.3 \frac{(\rho u_{pt}^2)}{2} N_p \quad (12.79)$$

where  $u_{pt}$  = the velocity through the ports  $w/\rho A_p$ , m/s,

$w$  = mass flow through the ports, kg/s,

$A_p$  = area of the port =  $(\pi d_{pt}^2)/4$ , m<sup>2</sup>,

$d_{pt}$  = port diameter, m,

$N_p$  = number of passes.

### Example 12.13

Investigate the use of a gasketed plate heat exchanger for the duty set out in Example 12.1: cooling methanol using brackish water as the coolant. Titanium plates are to be specified, to resist corrosion by the saline water.

#### Summary of Example 12.1

Cool 100,000 kg/h of methanol from 95°C to 40°C, duty 4340 kW. Cooling water inlet temperature 25°C and outlet temperature 40°C. Flow-rates: methanol 27.8 kg/s, water 68.9 kg/s.

Physical properties:	Methanol	Water
Density, kg/m <sup>3</sup>	750	995
Viscosity, mN m <sup>-2</sup> s	3.4	0.8
Prandtl number	5.1	5.7

Logarithmic mean temperature difference 31°C.

**Solution**

NTU, based on the maximum temperature difference

$$= \frac{95 - 40}{31} = 1.8$$

Try a 1 : 1 pass arrangement.

From Figure 12.62,  $F_t = 0.96$

From Table 12.2 take the overall coefficient, light organic - water, to be  $2000 \text{ Wm}^{-2}\text{C}^{-1}$ .

$$\text{Then, area required} = \frac{4340 \times 10^3}{2000 \times 0.96 \times 31} = 72.92 \text{ m}^2$$

Select an effective plate area of  $0.75 \text{ m}^2$ , effective length 1.5 m and width 0.5 m; these are typical plate dimensions. The actual plate size will be larger to accommodate the gasket area and ports.

$$\begin{aligned} \text{Number of plates} &= \text{total heat transfer area} / \text{effective area of one plate} \\ &= 72.92 / 0.75 = 97 \end{aligned}$$

No need to adjust this, 97 will give an even number of channels per pass, allowing for an end plate.

Number of channels per pass =  $(97 - 1) / 2 = 48$

Take plate spacing as 3 mm, a typical value, then:

channel cross-sectional area =  $3 \times 10^{-3} \times 0.5 = 0.0015 \text{ m}^2$

and hydraulic mean diameter =  $2 \times 3 \times 10^{-3} = 6 \times 10^{-3} \text{ m}$

**Methanol**

$$\text{Channel velocity} = \frac{27.8}{750} \times \frac{1}{0.0015} \times \frac{1}{48} = 0.51 \text{ m/s}$$

$$Re = \frac{\rho u_p d_e}{\mu} = \frac{750 \times 0.51 \times 6 \times 10^{-3}}{0.34 \times 10^{-3}} = 6750$$

$$Nu = 0.26(6750)^{0.65} \times 5.1^{0.4} = 153.8 \quad (12.77)$$

$$h_p = 153.8(0.19 / 6 \times 10^{-3}) = 4870 \text{ Wm}^{-2}\text{C}^{-1}$$

**Brackish water**

$$\text{Channel velocity} = \frac{68.9}{995} \times \frac{1}{0.0015} \times \frac{1}{48} = 0.96 \text{ m/s}$$

$$Re = \frac{955 \times 0.96 \times 6 \times 10^{-3}}{0.8 \times 10^{-3}} = 6876$$

$$Nu = 0.26(6876)^{0.65} \times 5.7^{0.4} = 162.8 \quad (12.77)$$

$$h_p = 162.8(0.59 / 6 \times 10^{-3}) = 16,009 \text{ Wm}^{-2}\text{C}^{-1}$$

**Overall coefficient**

From Table 12.9, take the fouling factors (coefficients) as: brackish water (seawater)  $6000 \text{ Wm}^{-2}\text{C}^{-1}$  and methanol (light organic)  $10,000 \text{ Wm}^{-2}\text{C}^{-1}$ .

Take the plate thickness as 0.75 mm. Thermal conductivity of titanium 21  $\text{Wm}^{-1}\text{C}^{-1}$ .

$$\frac{1}{U} = \frac{1}{4870} + \frac{1}{10,000} + \frac{0.75 \times 10^{-3}}{21} + \frac{1}{16,009} + \frac{1}{6000}$$

$$U = \underline{1754} \text{ Wm}^{-2}\text{C}^{-1}, \text{ too low}$$

Increase the number of channels per pass to 60; giving  $(2 \times 60) + 1 = 121$  plates.

Then, methanol channel velocity =  $0.51 \times (48/60) = 0.41 \text{ m/s}$ , and  $Re = 5400$ .

Cooling water channel velocity =  $0.96 \times (48/60) = 0.77 \text{ m/s}$ , and  $Re = 5501$ .

Giving,  $h_p = 4215 \text{ Wm}^{-2}\text{C}^{-1}$  for methanol, and  $13,846 \text{ Wm}^{-2}\text{C}^{-1}$  for water.

Which gives an overall coefficient of  $\underline{1634} \text{ Wm}^{-2}\text{C}^{-1}$ .

Overall coefficient required  $2000 \times 48/60 = \underline{1600} \text{ Wm}^{-2}\text{C}^{-1}$ , so 60 plates per pass should be satisfactory.

**Pressure drops***Methanol*

$$J_f = 0.60(5400)^{-0.3} = 0.046$$

Path length = plate length  $\times$  number of passes =  $1.5 \times 1 = 1.5 \text{ m}$ .

$$\Delta P_p = 8 \times 0.046 \left( \frac{1.5}{6 \times 10^{-3}} \right) \times 750 \times \frac{0.41^2}{2} = 5799 \text{ N/m}^2 \quad (12.78)$$

Port pressure loss, take port diameter as 100 mm, area =  $0.00785 \text{ m}^2$ .

Velocity through port =  $(27.8/750)/0.00785 = 4.72 \text{ m/s}$ .

$$\Delta P_{pt} = 1.3 \times \frac{750 \times 4.72^2}{2} = 10,860 \text{ N/m}^2 \quad (12.79)$$

Total pressure drop =  $5799 + 10,860 = \underline{16,659} \text{ N/m}^2$ , 0.16 bar.

*Water*

$$J_f = 0.6(5501)^{-0.3} = 0.045$$

Path length = plate length  $\times$  number of passes =  $1.5 \times 1 = 1.5 \text{ m}$ .

$$\Delta P_p = 8 \times 0.045 \times \left( \frac{1.5}{6 \times 10^{-3}} \right) \times 995 \times \frac{0.77^2}{2} = 26,547 \text{ N/m}^2 \quad (12.78)$$

Velocity through port =  $(68.9/995)/0.0078 = 8.88 \text{ m/s}$  (rather high)

$$\Delta P_{pt} = 1.3 \times \frac{995 \times 8.88^2}{2} = 50,999 \text{ N/m}^2 \quad (12.79)$$

Total pressure drop =  $26,547 + 50,999 = \underline{\underline{77,546}}$  N/m<sup>2</sup>, 0.78 bar

Could increase the port diameter to reduce the pressure drop.

The trial design should be satisfactory, so a plate heat exchanger could be considered for this duty.

### 12.12.2. Welded plate

Welded plate heat exchangers use plates similar to those in gasketed plate exchangers but the plate edges are sealed by welding. This increases the pressure and temperature rating to up to 80 bar and temperatures in excess of 500°C. They retain the advantages of plate heat exchangers (compact size and good rates of heat transfer) whilst giving security against leakage. An obvious disadvantage is that the exchangers cannot be dismantled for cleaning. So, their use is restricted to specialised applications where fouling is not a problem. The plates are fabricated in a variety of materials.

A combination of gasketed and welded plate construction is also used. An aggressive process fluid flowing between welded plates and a benign process stream, or service stream, between gasketed plates.

### 12.12.3. Plate-fin

Plate-fin exchangers consist essentially of plates separated by corrugated sheets, which form the fins. They are made up in a block and are often referred to as matrix exchangers; see Figure 12.63. They are usually constructed of aluminium and joined and sealed by brazing. The main application of plate-fin exchangers has been in the cryogenics industries, such as air separation plants, where large heat transfer surface areas are needed. They are now finding wider applications in the chemical processes industry, where large surface area, compact, exchangers are required. Their compact size and low weight have led to some use in off-shore applications. The brazed aluminium construction is limited to pressures up to around 60 bar and temperatures up to 150°C. The units cannot be mechanically cleaned, so their use is restricted to clean process and service steams. The

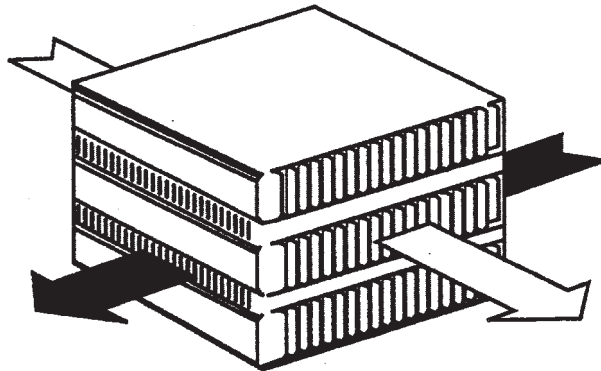


Figure 12.63. Plate-fin exchanger

construction and design of plate-fin exchangers and their applications are discussed by Saunders (1988) and Burley (1991), and their use in cryogenic service by Lowe (1987).

#### 12.12.4. Spiral heat exchangers

A spiral heat exchanger can be considered as a plate heat exchanger in which the plates are formed into a spiral. The fluids flow through the channels formed between the plates. The exchanger is made up from long sheets, between 150 to 1800 mm wide, formed into a pair of concentric spiral channels. The channels are closed by gasketed end-plates bolted to an outer case. Inlet and outlet nozzles are fitted to the case and connect to the channels, see Figure 12.64. The gap between the sheets varies between 4 to 20 mm; depending on the size of the exchanger and the application. They can be fabricated in any material that can be cold-worked and welded.

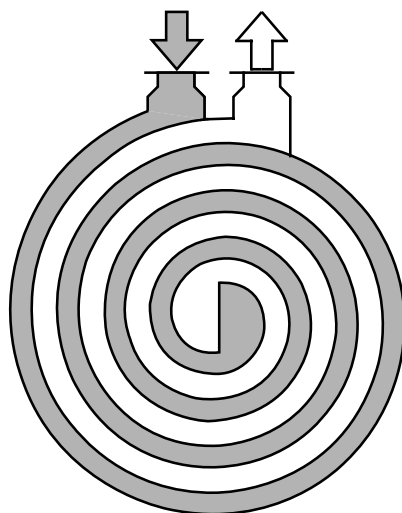


Figure 12.64. Spiral heat exchanger

Spiral heat exchangers are compact units: a unit with around 250 m<sup>2</sup> area occupying a volume of approximately 10 m<sup>3</sup>. The maximum operating pressure is limited to 20 bar and the temperature to 400°C.

For a given duty, the pressure drop over a spiral heat exchanger will usually be lower than that for the equivalent shell-and-tube exchanger. Spiral heat exchangers give true counter-current flow and can be used where the temperature correction factor  $F_t$  for a shell-and-tube exchanger would be too low; see Section 12.6. Because they are easily cleaned and the turbulence in the channels is high, spiral heat exchangers can be used for very dirty process fluids and slurries.

The correlations for flow in conduits can be used to estimate the heat transfer coefficient and pressure drop in the channels; using the hydraulic mean diameter as the characteristic dimension.

The design of spiral heat exchangers is discussed by Minton (1970)

### 12.13. DIRECT-CONTACT HEAT EXCHANGERS

In direct-contact heat exchange the hot and cold streams are brought into contact without any separating wall, and high rates of heat transfer are achieved.

Applications include: reactor off-gas quenching, vacuum condensers, cooler-condensers, desuperheating and humidification. Water-cooling towers are a particular example of direct-contact heat exchange. In direct-contact cooler-condensers the condensed liquid is frequently used as the coolant, Figure 12.65.

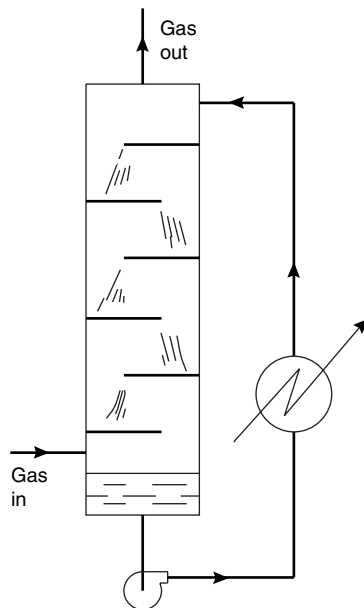


Figure 12.65. Typical direct-contact cooler (baffle plates)

Direct-contact heat exchangers should be considered whenever the process stream and coolant are compatible. The equipment used is basically simple and cheap, and is suitable for use with heavily fouling fluids and with liquids containing solids; spray chambers, spray columns, and plate and packed columns are used.

There is no general design method for direct contact exchangers. Most applications will involve the transfer of latent heat as well as sensible heat, and the process is one of simultaneous heat and mass transfer. When the approach to thermal equilibrium is rapid, as it will be in many applications, the size of the contacting vessel is not critical and the design can be based on experience with similar processes. For other situations the designer must work from first principles, setting up the differential equations for mass and heat transfer, and using judgement in making the simplifications necessary to achieve a solution. The design procedures used are analogous to those for gas absorption and distillation. The rates of heat transfer will be high; with coefficients for packed columns typically in the range 2000 to 20,000  $\text{W/m}^3\text{C}$  (i.e. per cubic meter of packing).

The design and application of direct-contact heat exchangers is discussed by Fair (1961, 1972*a*, 1972*b*), and Chen-Chia and Fair (1989), they give practical design methods and data for a range of applications.

The design of water-cooling towers, and humidification, is covered in Volume 1, Chapter 13. The same basic principles will apply to the design of other direct-contact exchangers.

## 12.14. FINNED TUBES

Fins are used to increase the effective surface area of heat-exchanger tubing. Many different types of fin have been developed, but the plain transverse fin shown in Figure 12.66 is the most commonly used type for process heat exchangers. Typical fin dimensions are: pitch 2.0 to 4.0 mm, height 12 to 16 mm; ratio of fin area to bare tube area 15 : 1 to 20 : 1.

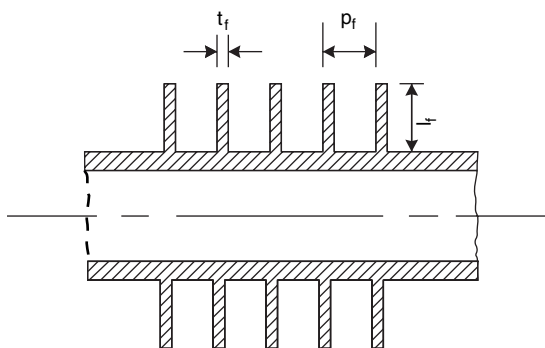


Figure 12.66. Finned tube

Finned tubes are used when the heat-transfer coefficient on the outside of the tube is appreciably lower than that on the inside; as in heat transfer from a liquid to a gas, such as in air-cooled heat exchangers.

The fin surface area will not be as effective as the bare tube surface, as the heat has to be conducted along the fin. This is allowed for in design by the use of a fin effectiveness, or fin efficiency, factor. The basic equations describing heat transfer from a fin are derived in Volume 1, Chapter 9; see also Kern (1950). The fin effectiveness is a function of the fin dimensions and the thermal conductivity of the fin material. Fins are therefore usually made from metals with a high thermal conductivity; for copper and aluminium the effectiveness will typically be between 0.9 to 0.95.

When using finned tubes, the coefficients for the outside of the tube in equation 12.2 are replaced by a term involving fin area and effectiveness:

$$\frac{1}{h_o} + \frac{1}{h_{od}} = \frac{1}{E_f} \left( \frac{1}{h_f} + \frac{1}{h_{df}} \right) \frac{A_o}{A_f} \quad (12.80)$$

where  $h_f$  = heat-transfer coefficient based on the fin area,



- $h_{df}$  = fouling coefficient based on the fin area,  
 $A_o$  = outside area of the bare tube,  
 $A_f$  = fin area,  
 $E_f$  = fin effectiveness.

It is not possible to give a general correlation for the coefficient  $h_f$  covering all types of fin and fin dimensions. Design data should be obtained from the tube manufacturers for the particular type of tube to be used. Some information is given in Volume 1, Chapter 9. For banks of tubes in cross flow, with plain transverse fins, the correlation given by Briggs and Young (1963) can be used to make an approximate estimate of the fin coefficient.

$$Nu = 0.134Re^{0.681}Pr^{0.33} \left[ \frac{p_f - t_f}{l_f} \right]^{0.2} \left[ \frac{p_f}{t_f} \right]^{0.1134} \quad (12.81)$$

- where  $p_f$  = fin pitch,  
 $l_f$  = fin height,  
 $t_f$  = fin thickness.

The Reynolds number is evaluated for the bare tube (i.e. assuming that no fins exist).

Kern and Kraus (1972) give full details of the use of finned tubes in process heat exchangers design and design methods.

### **Low fin tubes**

Tubes with low transverse fins, about 1 mm high, can be used with advantage as replacements for plain tubes in many applications. The fins are formed by rolling, and the tube outside diameters are the same as those for standard plain tubes. Details are given in the manufacturer's data books, Wolverine (1984) and an electronic version of their design manual, www.wlv.com (2001); see also Webber (1960).

## **12.15. DOUBLE-PIPE HEAT EXCHANGERS**

One of the simplest and cheapest types of heat exchanger is the concentric pipe arrangement shown in Figure 12.67. These can be made up from standard fittings, and are useful where only a small heat-transfer area is required. Several units can be connected in series to extend their capacity.

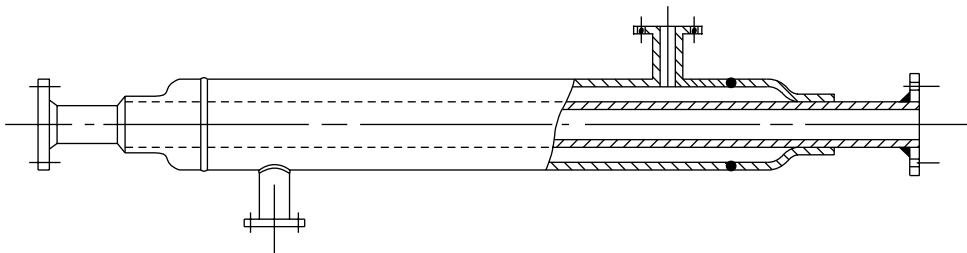


Figure 12.67. Double-pipe exchanger (constructed for weld fittings)

The correlation for forced convective heat transfer in conduits (equation 12.10) can be used to predict the heat transfer coefficient in the annulus, using the appropriate equivalent diameter:

$$d_e = \frac{4 \times \text{cross-sectional area}}{\text{wetted perimeter}} = \frac{4(d_2^2 - d_1^2)\frac{\pi}{4}}{\pi(d_2 + d_1)} = d_2 - d_1$$

where  $d_2$  is the inside diameter of the outer pipe and  $d_1$  the outside diameter of the inner pipe.

Some designs of double-pipe exchanger use inner tubes fitted with longitudinal fins.

## 12.16. AIR-COOLED EXCHANGERS

Air-cooled exchangers should be considered when cooling water is in short supply or expensive. They can also be competitive with water-cooled units even when water is plentiful. Frank (1978) suggests that in moderate climates air cooling will usually be the best choice for minimum process temperatures above 65°C, and water cooling for minimum processes temperatures below 50°C. Between these temperatures a detailed economic analysis would be necessary to decide the best coolant. Air-cooled exchangers are used for cooling and condensing.

Air-cooled exchangers consist of banks of finned tubes over which air is blown or drawn by fans mounted below or above the tubes (forced or induced draft). Typical units are shown in Figure 12.68. Air-cooled exchangers are packaged units, and would normally be selected and specified in consultation with the manufacturers. Some typical overall coefficients are given in Table 12.1. These can be used to make an approximate estimate of the area required for a given duty. The equation for finned tubes given in Section 12.14 can also be used.

The design and application of air-cooled exchangers is discussed by Rubin (1960), Lerner (1972), Brown (1978) and Mukherjee (1997). Design procedures are also given in the books by Kern (1950), Kern and Kraus (1972), and Kroger (2004). Lerner and Brown give typical values for the overall coefficient for a range of applications and provide methods for the preliminary sizing of air-cooled heat exchangers.

Details of the construction features of air-cooled exchangers are given by Ludwig (1965). The construction features of air-cooled heat exchangers are covered by the American Petroleum Institute standard, API 661.

## 12.17. FIRED HEATERS (FURNACES AND BOILERS)

When high temperatures and high flow rates are required, fired-heaters are used. Fired heaters are directly heated by the products of combustion of a fuel. The capacity of fired heaters ranges from 3 to 100 MW.

Typical applications of fired heaters are:

1. Process feed-stream heaters; such as the feed heaters for refinery crude columns (pipe stills); in which up to 60 per cent of the feed may be vaporised.
2. Reboilers for columns, using relatively small size direct-fired units.

3. Direct-fired reactors; for example, the pyrolysis of dichloroethane to form vinyl chloride.
4. Reformers for hydrogen production, giving outlet temperatures of 800–900°C.
5. Steam boilers.

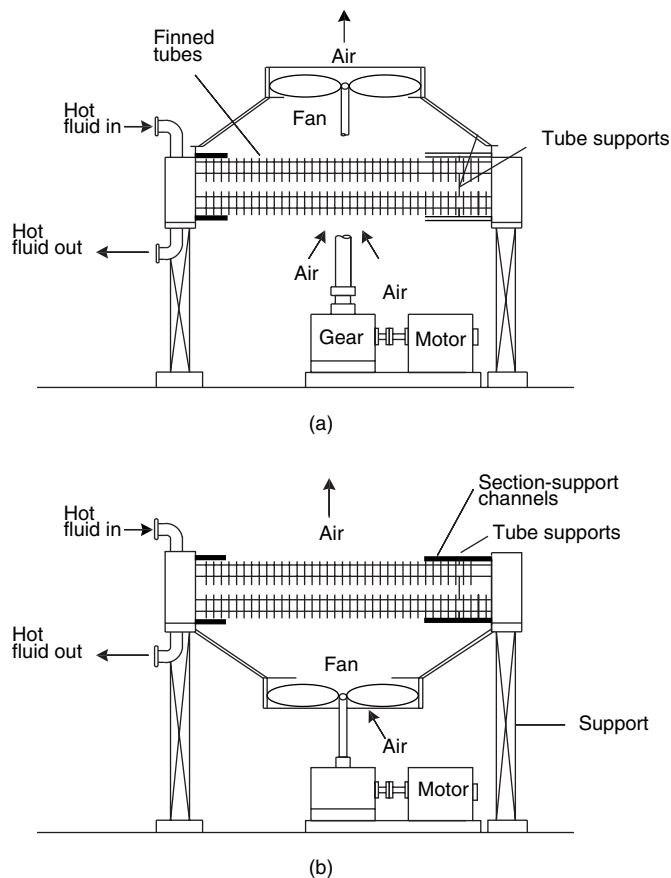


Figure 12.68. Air-cooled exchangers

### 12.17.1. Basic construction

Many different designs and layouts are used, depending on the application, see Bergman (1979a).

The basic construction consists of a rectangular or cylindrical steel chamber, lined with refractory bricks. Tubes are arranged around the wall, in either horizontal or vertical banks. The fluid to be heated flows through the tubes. Typical layouts are shown in Figure 12.69*a*, *b* and *c*. A more detailed diagram of a pyrolysis furnace is given in Figure 12.70.

Heat transfer to the tubes on the furnace walls is predominantly by radiation. In modern designs this radiant section is surmounted by a smaller section in which the combustion

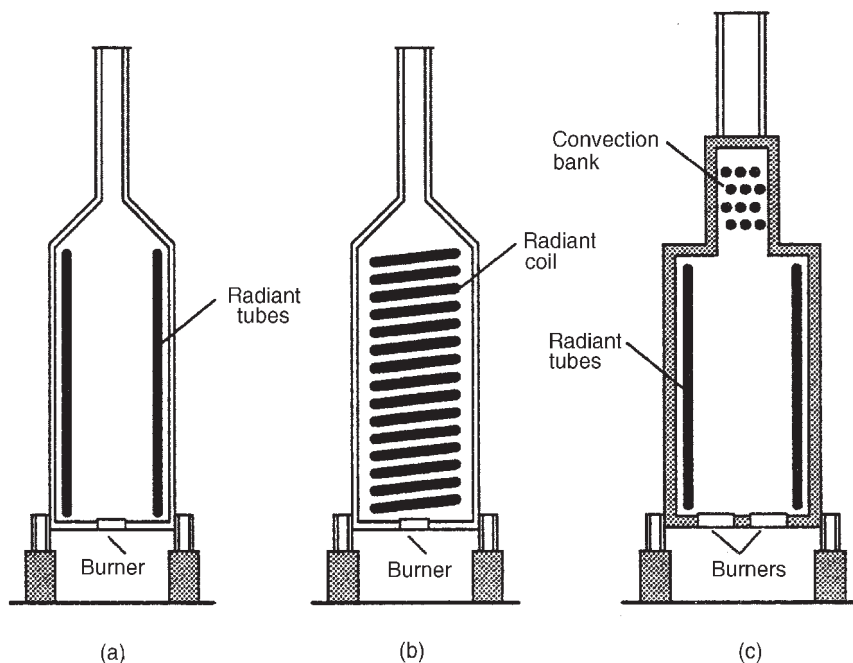


Figure 12.69. Fired heaters. (a) Vertical-cylindrical, all radiant (b) Vertical-cylindrical, helical coil (c) Vertical-cylindrical with convection section

gases flow over banks of tubes and transfer heat by convection. Extended surface tubes, with fins or pins, are used in the convection section to improve the heat transfer from the combustion gases. Plain tubes are used in the bottom rows of the convection section to act as a heat shield from the hot gases in the radiant section. Heat transfer in the shield section will be by both radiation and convection. The tube sizes used will normally be between 75 and 150 mm diameter. The tube size and number of passes used depending on the application and the process-fluid flow-rate. Typical tube velocities will be from 1 to 2 m/s for heaters, with lower rates used for reactors. Carbon steel is used for low temperature duties; stainless steel and special alloy steels for elevated temperatures. For high temperatures, a material that resists creep must be used.

The burners are positioned at base or sides of radiant section. Gaseous and liquid fuels are used. The combustion air may be preheated in tubes in the convection section.

### 12.17.2. Design

Computer programs for the design of fired heaters are available from commercial organizations; such as HTFS and HTRI, see Section 12.1. Manual calculation methods, suitable for the preliminary design of fired heaters, are given by Kern (1950), Wimpres (1978) and Evans (1980). A brief review of the factors to be considered is given in the following sections.

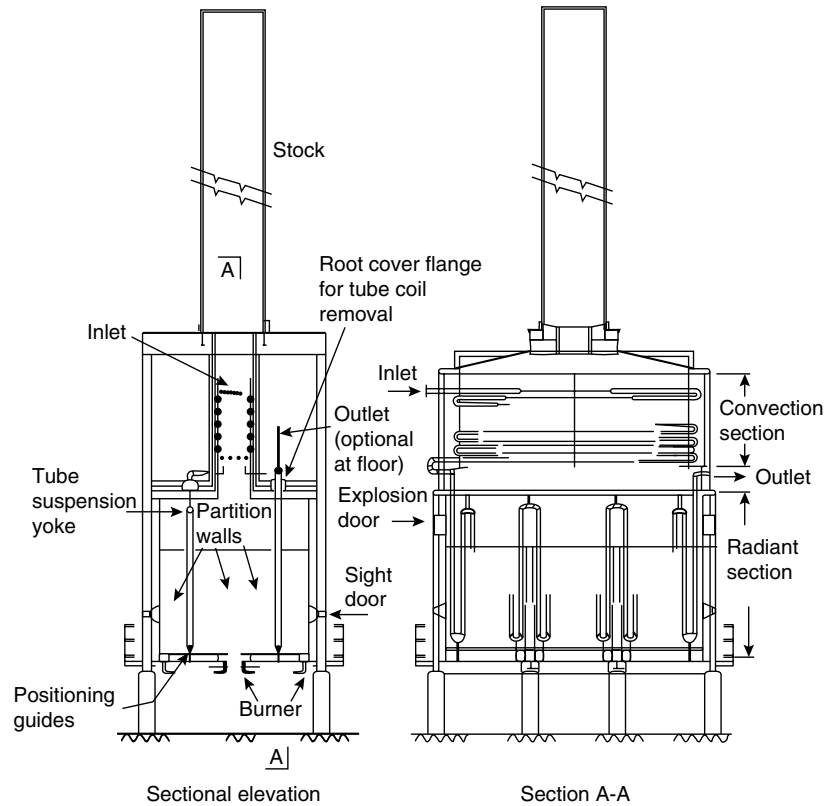


Figure 12.70. (Foster Wheeler) Multi-zoned pyrolysis furnace

### 12.17.3. Heat transfer

#### ***Radiant section***

Between 50 to 70 per cent of the total heat is transferred in the radiant section.

The gas temperature will depend on the fuel used and the amount of excess air. For gaseous fuels around 20% excess air is normally used, and 25% for liquid fuels.

Radiant heat transfer from a surface is governed by the Stefan-Boltzman equation, see Volume 1, Chapter 9.

$$q_r = \sigma T^4 \quad (12.82)$$

where  $q_r$  = radiant heat flux,  $\text{W/m}^2$

$\sigma$  = Stephen-Boltzman constant,  $5.67 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$

$T$  = temperature of the surface, K.

For the exchange of heat between the combustion gases and the hot tubes the equation can be written as:

$$Q_r = \sigma(\alpha A_{cp})F(T_g^4 - T_t^4) \quad (12.83)$$

where  $Q_r$  = radiant heat transfer rate, W

$A_{cp}$  = the “cold-plane” area of the tubes

= number of tubes  $\times$  the exposed length  $\times$  tube pitch

$\alpha$  = the absorption efficiency factor

$F$  = the radiation exchange factor

$T_g$  = temperature of the hot gases, K

$T_t$  = tube surface temperature, K

Part of the radiation from the hot combustion gases will strike the tubes and be absorbed, and part will pass through the spaces between the tubes and be radiated back into the furnace. If the tubes are in front of the wall, some of the radiation from the wall will also be absorbed by the tubes. This complex situation is allowed for by calculating what is known as the cold plane area of the tubes  $A_{cp}$ , and then applying the absorption efficiency factor  $\alpha$  to allow for the fact that the tube area will not be as effective as a plane area. The absorption efficiency factor is a function of the tube arrangement and will vary from around 0.4 for widely spaced tubes, to 1.0 for the theoretical situation when the tubes are touching. It will be around 0.7 to 0.8 when the pitch equals the tube diameter. Values for  $\alpha$  are available in handbooks for a range of tube arrangements; see Perry *et al.* (1997), and Wimpress (1978).

The radiation exchange factor  $F$  depends on the arrangement of the surfaces and their emissivity and absorptivity. Combustion gases are poor radiators, because only the carbon dioxide and water vapour, about 20 to 25 per cent of the total, will emit radiation in the thermal spectrum. For a fired heater the exchange factor will depend on the partial pressure and emissivity of these gases, and the layout of the heater. The partial pressure is dependent on the kind of fuel used, liquid or gas, and the amount of excess air. The gas emissivity is a function of temperature. Methods for estimating the exchange factor for typical furnace designs are given in the handbooks; see Perry *et al.* (1997), and Wimpress (1978).

The heat flux to the tubes in the radiant section will lie between 20 to 40 kW/m<sup>2</sup>, for most applications. A value of 30 kW/m<sup>2</sup> can be used to make a rough estimate of the tube area needed in this section.

A small amount of heat will be transferred to the tubes by convection in the radiant section, but as the superficial velocity of the gases will be low, the heat transfer coefficient will be low, around 10 Wm<sup>-2</sup>°C<sup>-1</sup>.

### **Convection section**

The combustion gases flow across the tube banks in the convection section and the correlations for cross-flow in tube banks can be used to estimate the heat transfer coefficient. The gas side coefficient will be low, and where extended surfaces are used an allowance must be made for the fin efficiency. Procedures are given in the tube vendors literature, and in handbooks, see Section 12.14, and Bergman (1978b).

The overall coefficient will depend on the gas velocity and temperature, and the tube size. Typical values range from 20 to 50 Wm<sup>-2</sup>°C<sup>-1</sup>.

The lower tubes in the shield bank in the convection section will receive heat by radiation from the radiant section. This can be allowed for by including the area of the lower row of tubes with the tubes in the radiant section.

#### 12.17.4. Pressure drop

Most of the pressure drop will occur in the convection section. The procedures for estimating the pressure drop across banks of tubes can be used to estimate the pressure drop in this section, see Section 12.9.4 and Volume 1, Chapter 9.

The pressure drop in the radiant section will be small compared with that across the convection section and can usually be neglected.

#### 12.17.5. Process-side heat transfer and pressure drop

The tube inside heat transfer coefficients and pressure drop can be calculated using the conventional methods for flow inside tubes; see Section 12.8, and Volume 1, Chapter 9. If the unit is being used as a vaporiser the existence of two-phase flow in some of the tubes must be taken into account. Bergman (1978b) gives a quick method for estimating two-phase pressure drop in the tubes of fired heaters.

Typical approach temperatures, flue gas to inlet process fluid, are around 100°C.

#### 12.17.6. Stack design

Most fired heaters operate with natural draft, and the stack height must be sufficient to achieve the flow of combustion air required and to remove the combustion products.

It is normal practice to operate with a slight vacuum throughout the heater, so that air will leak in through sight-boxes and dampers, rather than combustion products leak out. Typically, the aim would be to maintain a vacuum of around 2 mm water gauge just below the convection section.

The stack height required will depend on the temperature of the combustion gases leaving the convection section and the elevation of the site above sea level. The draft arises from the difference in density of the hot gases and the surrounding air.

The draft in millimetres of water (mm H<sub>2</sub>O) can be estimated using the equation:

$$P_d = 0.35(L_s)(p') \left[ \frac{1}{T_a} - \frac{1}{T_{ga}} \right] \quad (12.84)$$

where  $L_s$  = stack height, m

$p'$  = atmospheric pressure, millibar ( $\text{N/m}^2 \times 10^{-2}$ )

$T_a$  = ambient temperature, K

$T_{ga}$  = average flue-gas temperature, K

Because of heat losses, the temperature at the top of the stack will be around 80°C below the inlet temperature.

The frictional pressure loss in the stack must be added to the loss in the heater when estimating the stack draft required. This can be calculated using the usual methods for pressure loss in circular conduits, see Section 12.8. The mass velocity in the stack will be around 1.5 to 2 kg/m<sup>2</sup>. These values can be used to determine the cross-section needed.

An approximate estimate of the pressure losses in the convection section can be made by multiplying the velocity head ( $u^2/2g$ ) by factors for each restriction; typical values are given below:

- 0.2–0.5 for each row of plain tubes
- 1.0–2.0 for each row of finned tubes
- 0.5 for the stack entrance
- 1.0 for the stack exit
- 1.5 for the stack damper

### 12.17.7. Thermal efficiency

Modern fired heaters operate at thermal efficiencies of between 80 to 90 per cent, depending on the fuel and the excess air requirement. In some applications additional excess air may be used to reduce the flame temperature, to avoid overheating of the tubes.

Where the inlet temperature of the process fluid is such that the outlet temperature from the convection section would be excessive, giving low thermal efficiency, this excess heat can be used to preheat the air to the furnace. Tubes would be installed above the process fluid section in the convection section. Forced draft operation would be needed to drive the air flow through the preheat section.

Heat losses from the heater casing are normally between 1.5 to 2.5 per cent of the heat input.

## 12.18. HEAT TRANSFER TO VESSELS

The simplest way to transfer heat to a process or storage vessel is to fit an external jacket, or an internal coil.

### 12.18.1. Jacketed vessels

#### *Conventional jackets*

The most commonly used type jacket is that shown in Figure 12.71. It consists of an outer cylinder which surrounds part of the vessel. The heating or cooling medium circulates in the annular space between the jacket and vessel walls and the heat is transferred through the wall of the vessel. Circulation baffles are usually installed in the annular space to increase the velocity of the liquid flowing through the jacket and improve the heat transfer coefficient, see Figure 12.72a. The same effect can be obtained by introducing the fluid through a series of nozzles spaced down the jacket. The momentum of the jets issuing from the nozzles sets up a swirling motion in the jacket liquid; Figure 12.72d.

The spacing between the jacket and vessel wall will depend on the size of the vessel, but will typically range from 50 mm for small vessels to 300 mm for large vessels.

#### *Half-pipe jackets*

Half-pipe jackets are formed by welding sections of pipe, cut in half along the longitudinal axis, to the vessel wall. The pipe is usually wound round the vessel in a helix; Figure 12.72c.



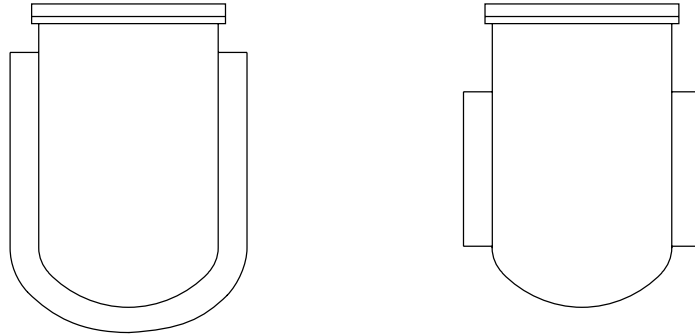


Figure 12.71. Jacketed vessel

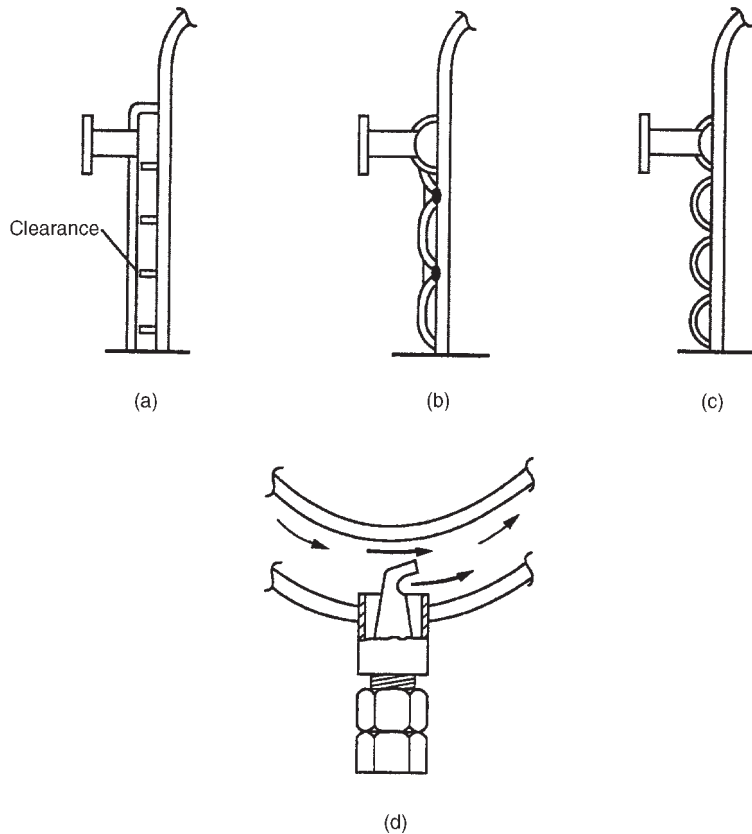


Figure 12.72. Jacketed vessels. (a) Spirally baffled jacket (b) Dimple jacket (c) Half-pipe jacket (d) Agitation nozzle

The pitch of the coils and the area covered can be selected to provide the heat transfer area required. Standard pipe sizes are used; ranging from 60 to 120 mm outside diameter. The half-pipe construction makes a strong jacket capable of withstanding pressure better than the conventional jacket design.

### ***Dimpled jackets***

Dimpled jackets are similar to the conventional jackets but are constructed of thinner plates. The jacket is strengthened by a regular pattern of hemispherical dimples pressed into the plate and welded to the vessel wall, Figure 12.72*b*.

### ***Jacket selection***

Factors to consider when selecting the type of jacket to use are listed below:

1. Cost: in terms of cost the designs can be ranked, from cheapest to most expensive, as:
  - simple, no baffles
  - agitation nozzles
  - spiral baffle
  - dimple jacket
  - half-pipe jacket
2. Heat transfer rate required: select a spirally baffled or half-pipe jacket if high rates are required.
3. Pressure: as a rough guide, the pressure rating of the designs can be taken as:
  - jackets, up to 10 bar
  - dimpled jackets, up to 20 bar
  - half-pipe, up to 70 bar.

So, half-pipe jackets would be used for high pressure.

### ***Jacket heat transfer and pressure drop***

The heat transfer coefficient to the vessel wall can be estimated using the correlations for forced convection in conduits, such as equation 12.11. The fluid velocity and the path length can be calculated from the geometry of the jacket arrangement. The hydraulic mean diameter (equivalent diameter,  $d_e$ ) of the channel or half-pipe should be used as the characteristic dimension in the Reynolds and Nusselt numbers; see Section 12.8.1.

In dimpled jackets a velocity of 0.6 m can be used to estimate the heat transfer coefficient. A method for calculating the heat transfer coefficient for dimpled jackets is given by Makovitz (1971).

The coefficients for jackets using agitation nozzles will be similar to that given by using baffles. A method for calculating the heat transfer coefficient using agitation nozzles is given by Bolliger (1982).

To increase heat transfer rates, the velocity through a jacket can be increased by recirculating the cooling or heating liquid.

For simple jackets without baffles, heat transfer will be mainly by natural convection and the heat transfer coefficient will range from 200 to 400  $\text{Wm}^{-2}\text{C}^{-1}$ .

### **12.18.2. Internal coils**

The simplest and cheapest form of heat transfer surface for installation inside a vessel is a helical coil; see Figure 12.73. The pitch and diameter of the coil can be made to suit the

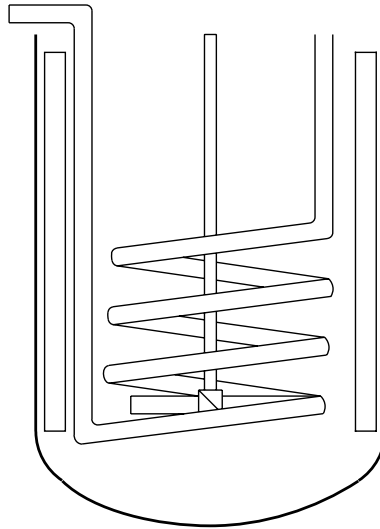


Figure 12.73. Internal coils

application and the area required. The diameter of the pipe used for the coil is typically equal to  $D_v/30$ , where  $D_v$  is the vessel diameter. The coil pitch is usually around twice the pipe diameter. Small coils can be self supporting, but for large coils some form of supporting structure will be necessary. Single or multiple turn coils are used.

### ***Coil heat transfer and pressure drop***

The heat transfer coefficient at the inside wall and pressure drop through the coil can be estimated using the correlations for flow through pipes; see Section 12.8 and Volume 1, Chapters 3 and 9. Correlations for forced convection in coiled pipes are also given in the Engineering Sciences Data Unit Design Guide, ESDU 78031 (2001).

### **12.18.3. Agitated vessels**

Unless only small rates of heat transfer are required, as when maintaining the temperature of liquids in storage vessels, some form of agitation will be needed. The various types of agitator used for mixing and blending described in Chapter 10, Section 10.11.2, are also used to promote heat transfer in vessels. The correlations used to estimate the heat transfer coefficient to the vessel wall, or to the surface of coils, have the same form as those used for forced convection in conduits, equation 12.10. The fluid velocity is replaced by a function of the agitator diameter and rotational speed,  $D \times N$ , and the characteristic dimension is the agitator diameter.

$$Nu = CRe^a Pr^b \left( \frac{\mu}{\mu_w} \right)^c \quad (12.10)$$

For agitated vessels:

$$\frac{h_v D}{k_f} = C \left( \frac{ND^2 \rho}{\mu} \right)^a \left( \frac{C_p \mu}{k_f} \right)^b \left( \frac{\mu}{\mu_w} \right)^c \quad (12.85)$$

where  $h_v$  = heat transfer coefficient to vessel wall or coil,  $\text{Wm}^{-2}\text{°C}^{-1}$

$D$  = agitator diameter, m

$N$  = agitator, speed, rps (revolutions per second)

$\rho$  = liquid density,  $\text{kg/m}^3$

$k_f$  = liquid thermal conductivity,  $\text{Wm}^{-1}\text{°C}^{-1}$

$C_p$  = liquid specific heat capacity,  $\text{J kg}^{-1}\text{°C}^{-1}$

$\mu$  = liquid viscosity,  $\text{Nm}^{-2}\text{s}$ .

The values of constant  $C$  and the indices  $a$ ,  $b$  and  $c$  depend on the type of agitator, the use of baffles, and whether the transfer is to the vessel wall or to coils. Some typical correlations are given below.

Baffles will normally be used in most applications.

1. Flat blade paddle, baffled or unbaffled vessel, transfer to vessel wall,  $Re < 4000$ :

$$Nu = 0.36Re^{0.67} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.86a)$$

2. Flat blade disc turbine, baffled or unbaffled vessel, transfer to vessel wall,  $Re < 400$ :

$$Nu = 0.54Re^{0.67} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.86b)$$

3. Flat blade disc turbine, baffled vessel, transfer to vessel wall,  $Re > 400$ :

$$Nu = 0.74Re^{0.67} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.86c)$$

4. Propeller, 3 blades, transfer to vessel wall,  $Re > 5000$ :

$$Nu = 0.64Re^{0.67} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.86d)$$

5. Turbine, flat blades, transfer to coil, baffled,  $Re$ , 2000–700,000:

$$Nu = 1.10Re^{0.62} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.86e)$$

6. Paddle, flat blades, transfer to coil, baffled,

$$Nu = 0.87Re^{0.62} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (12.86f)$$

More comprehensive design data is given by: Uhl and Gray (1967), Wilkinson and Edwards (1972), Penny (1983) and Fletcher (1987).

**Example 12.14**

A jacketed, agitated reactor consists of a vertical cylinder 1.5 m diameter, with a hemispherical base and a flat, flanged, top. The jacket is fitted to the cylindrical section only and extends to a height of 1 m. The spacing between the jacket and vessel walls is 75 mm. The jacket is fitted with a spiral baffle. The pitch between the spirals is 200 mm.

The jacket is used to cool the reactor contents. The coolant used is chilled water at 10°C; flow-rate 32,500 kg/h, exit temperature 20°C.

Estimate the heat transfer coefficient at the outside wall of the reactor and the pressure drop through the jacket.

**Solution**

The baffle forms a continuous spiral channel, section 75 mm × 200 mm.

$$\text{Number of spirals} = \text{height of jacket/pitch} = \frac{1}{200} \times 10^{-3} = 5$$

$$\text{Length of channel} = 5 \times \pi \times 1.5 = 23.6 \text{ m}$$

$$\text{Cross-sectional area of channel} = (75 \times 200) \times 10^{-6} = 15 \times 10^{-3} \text{ m}^2$$

$$\begin{aligned} \text{Hydraulic mean diameter, } d_e &= \frac{4 \times \text{cross-sectional area}}{\text{wetted perimeter}} \\ &= \frac{4 \times (75 \times 200)}{2(75 + 200)} = 109 \text{ mm} \end{aligned}$$

Physical properties at mean temperature of 15°C, from steam tables:  $\rho = 999 \text{ kg/m}^3$ ,  $\mu = 1.136 \text{ mNm}^{-2}\text{s}$ ,  $Pr = 7.99$ ,  $k_f = 595 \times 10^{-3} \text{ Wm}^{-1} \text{ C}^{-1}$ .

$$\text{Velocity through channel, } u = \frac{32,500}{3600} \times \frac{1}{999} \times \frac{1}{15 \times 10^{-3}} = 0.602 \text{ m/s}$$

$$\text{Re} = \frac{999 \times 0.602 \times 109 \times 10^{-3}}{1.136 \times 10^{-3}} = 57,705$$

Chilled water is not viscous so use equation 12.11 with  $C = 0.023$ , and neglect the viscosity correction term.

$$Nu = 0.023Re^{0.8}Pr^{0.33} \quad (12.11)$$

$$h_j \times \frac{109 \times 10^{-3}}{595 \times 10^{-3}} = 0.023(57,705)^{0.8}(7.99)^{0.33}$$

$$h_j = \underline{\underline{1606}} \text{ Wm}^{-2}\text{C}^{-1}$$

Use equation 12.18 for estimating the pressure drop, taking the friction factor from Figure 12.24. As the hydraulic mean diameter will be large compared to the roughness of the jacket surface, the relative roughness will be comparable with that for heat exchanger tubes. The relative roughness of pipes and channels and the effect on the friction factor is covered in Volume 1, Chapter 3.

From Figure 12.24, for  $Re = 5.8 \times 10^4$ ,  $j_f = 3.2 \times 10^{-3}$

$$\Delta P = 8j_f \left( \frac{L}{d_e} \right) \rho \frac{u^2}{2} \quad (12.18)$$

$$\begin{aligned} \Delta P &= 8 \times 3.2 \times 10^{-3} \left( \frac{23.6}{109} \times 10^{-3} \right) 999 \times \frac{0.602^2}{2} \\ &= \underline{\underline{1003}} \text{ N/m}^2 \end{aligned}$$

### Example 12.15

The reactor described in Example 12.12 is fitted with a flat blade disc turbine agitator 0.6 m diameter, running at 120 rpm. The vessel is baffled and is constructed of stainless steel plate 10 mm thick.

The physical properties of the reactor contents are:

$$\begin{aligned} \rho &= 850 \text{ kg/m}^3, \quad \mu = 80 \text{ mNm}^{-2}\text{s}, \quad k_f = 400 \times 10^{-3} \text{ Wm}^{-1}\text{C}^{-1}, \\ C_p &= 2.65 \text{ kJ kg}^{-1}\text{C}^{-1}. \end{aligned}$$

Estimate the heat transfer coefficient at the vessel wall and the overall coefficient in the clean condition.

### Solution

Agitator speed (revs per sec) =  $1200/60 = 2 \text{ s}^{-1}$

$$\begin{aligned} Re &= \frac{\rho ND^2}{\mu} = \frac{850 \times 2 \times 0.6^2}{80 \times 10^{-3}} = 7650 \\ Pr &= \frac{C_p \mu}{k_f} = \frac{2.65 \times 10^3 \times 80 \times 10^{-3}}{400 \times 10^{-3}} = 530 \end{aligned}$$

For a flat blade turbine use equation 12.86c:

$$Nu = 0.74 Re^{0.67} Pr^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14}$$

Neglect the viscosity correction term:

$$\begin{aligned} \frac{h_v \times 0.6}{400 \times 10^{-3}} &= 0.74(7650)^{0.67} (530)^{0.33} \\ h_v &= 1564 \text{ Wm}^{-2}\text{C}^{-1} \end{aligned}$$

Taking the thermal conductivity of stainless steel as  $16 \text{ Wm}^{-1}\text{C}^{-1}$  and the jacket coefficient from Example 12.12.

$$\begin{aligned} \frac{1}{U} &= \frac{1}{1606} + \frac{10 \times 10^{-3}}{16} + \frac{1}{1564} \\ U &= 530 \text{ Wm}^{-2}\text{C}^{-1} \end{aligned}$$

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## 12.20. NOMENCLATURE

		Dimensions in $MLT\theta$
$A$	Heat transfer area	$L^2$
$A_{cp}$	Cold-plane area of tubes	$L^2$
$A_o$	Clearance area between bundle and shell	$L^2$
$A_f$	Fin area	$L^2$
$A_L$	Total leakage area	$L^2$
$A_o$	Outside area of bare tube	$L^2$
$A_p$	Area of a port plate heat exchanger	$L^2$
$A_s$	Cross-flow area between tubes	$L^2$
$A_{sb}$	Shell-to-baffle clearance area	$L^2$
$A_{tb}$	Tube-to-baffle clearance area	$L^2$
$a$	Index in equation 12.10	—
$B_c$	Baffle cut	—
$B_b$	Bundle cut	—
$b$	Index in equation 12.10	—
$C$	Constant in equation 12.10	—
$C_p$	Heat capacity at constant pressure	$L^2T^{-2}\theta^{-1}$
$C_{pg}$	Heat capacity of gas	$L^2T^{-2}\theta^{-1}$
$C_{pl}$	Heat capacity of liquid phase	$L^2T^{-2}\theta^{-1}$
$c$	Index in equation 12.10	—
$c_s$	Shell-to-baffle diametrical clearance	$L$
$c_t$	Tube-to-baffle diametrical clearance	$L$
$D$	Agitator diameter	$L$
$D_b$	Bundle diameter	$L$
$D_s$	Shell diameter	$L$
$D_v$	Vessel diameter	$L$
$d_e$	Equivalent diameter	$L$
$d_i$	Tube inside diameter	$L$
$d_{pt}$	Diameter of the ports in the plates of a plate heat exchanger	$L$
$d_o$	Tube outside diameter	$L$
$d_1$	Outside diameter of inner of concentric tubes	$L$
$d_2$	Inside diameter of outer of concentric tubes	$L$
$E_f$	Fin efficiency	—
$F$	Radiation exchange factor	—
$F_b$	Bypass correction factor, heat transfer	—
$F'_b$	Bypass correction factor, pressure drop	—
$F_L$	Leakage correction factor, heat transfer	—
$F'_L$	Leakage correction factor, pressure drop	—
$F_n$	Tube row correction factor	—
$F_t$	Log mean temperature difference correction factor	—
$F_w$	Window effect correction factor	—
$f_c$	Two-phase flow factor	—

$f_m$	Temperature correction factor for mixtures	—
$f_s$	Nucleate boiling suppression factor	—
$G$	Total mass flow-rate per unit area	$ML^{-2}T^{-1}$
$G_p$	Mass flow-rate per unit cross-sectional area between plates	$ML^{-2}T^{-1}$
$G_s$	Shell-side mass flow-rate per unit area	$ML^{-2}T^{-1}$
$G_t$	Tube-side mass flow-rate per unit area	$ML^{-2}T^{-1}$
$g$	Gravitational acceleration	$LT^{-2}$
$H_b$	Height from baffle chord to top of tube bundle	L
$H_c$	Baffle cut height	L
$H_s$	Sensible heat of stream	$ML^2T^{-3}$
$H_t$	Total heat of stream (sensible + latent)	$ML^2T^{-3}$
$h_c$	Heat-transfer coefficient in condensation	$MT^{-3}\theta^{-1}$
$(h_c)_1$	Mean condensation heat-transfer coefficient for a single tube	$MT^{-3}\theta^{-1}$
$(h_c)_b$	Heat-transfer coefficient for condensation on a horizontal tube bundle	$MT^{-3}\theta^{-1}$
$(h_c)_{N_r}$	Mean condensation heat-transfer coefficient for a tube in a row of tubes	$MT^{-3}\theta^{-1}$
$(h_c)_v$	Heat-transfer coefficient for condensation on a vertical tube	$MT^{-3}\theta^{-1}$
$(h_c)_{BK}$	Condensation coefficient from Boko-Kruzhilin correlation	$MT^{-3}\theta^{-1}$
$(h_c)_s$	Condensation heat transfer coefficient for stratified flow in tubes	$MT^{-3}\theta^{-1}$
$h'_c$	Local condensing film coefficient, partial condenser	$MT^{-3}\theta^{-1}$
$h_{cb}$	Convective boiling-heat transfer coefficient	$MT^{-3}\theta^{-1}$
$h_{cg}$	Local effective cooling-condensing heat-transfer coefficient, partial condenser	$MT^{-3}\theta^{-1}$
$h_{df}$	Fouling coefficient based on fin area	$MT^{-3}\theta^{-1}$
$h_f$	Heat-transfer coefficient based on fin area	$MT^{-3}\theta^{-1}$
$h_{fb}$	Film boiling heat-transfer coefficient	$MT^{-3}\theta^{-1}$
$h'_{fc}$	Forced-convection coefficient in equation 12.67	$MT^{-3}\theta^{-1}$
$h'_g$	Local sensible-heat-transfer coefficient, partial condenser	$MT^{-3}\theta^{-1}$
$h_i$	Film heat-transfer coefficient inside a tube	$MT^{-3}\theta^{-1}$
$h'_i$	Inside film coefficient in Boyko-Kruzhilin correlation	$MT^{-3}\theta^{-1}$
$h_{id}$	Fouling coefficient on inside of tube	$MT^{-3}\theta^{-1}$
$h_{nb}$	Nucleate boiling-heat-transfer coefficient	$MT^{-3}\theta^{-1}$
$h'_{nb}$	Nucleate boiling coefficient in equation 12.67	$MT^{-3}\theta^{-1}$
$h_o$	Heat-transfer coefficient outside a tube	$MT^{-3}\theta^{-1}$
$h_{oc}$	Heat-transfer coefficient for cross flow over an ideal tube bank	$MT^{-3}\theta^{-1}$
$h_{od}$	Fouling coefficient on outside of tube	$MT^{-3}\theta^{-1}$
$h_p$	Heat-transfer coefficient in a plate heat exchanger	$MT^{-3}\theta^{-1}$
$h_s$	Shell-side heat-transfer coefficient	$MT^{-3}\theta^{-1}$
$h_v$	Heat transfer coefficient to vessel wall or coil	$MT^{-3}\theta^{-1}$
$j_h$	Heat transfer factor defined by equation 12.14	—
$j_H$	Heat-transfer factor defined by equation 12.15	—
$j_f$	Friction factor	—
$K_1$	Constant in equation 12.3, from Table 12.4	—
$K_2$	Constant in equation 12.61	—
$K_b$	Constant in equation 12.74	—
$k_f$	Thermal conductivity of fluid	$MLT^{-3}\theta^{-1}$
$k_L$	Thermal conductivity of liquid	$MLT^{-3}\theta^{-1}$
$k_v$	Thermal conductivity of vapour	$MLT^{-3}\theta^{-1}$
$k_w$	Thermal conductivity of tube wall material	$MLT^{-3}\theta^{-1}$
$L'$	Effective tube length	L
$L_p$	Path length in a plate heat exchanger	L
$L_s$	Stack height	L
$l_B$	Baffle spacing (pitch)	L
$l_f$	Fin height	L
$N$	Rotational speed	$T^{-1}$
$N_b$	Number of baffles	—
$N_c$	Number of tubes in cross flow zone	—

$N'_c$	Number of tube rows crossed from end to end of shell	—
$N_{cv}$	Number of constrictions crossed	—
$N_p$	Number of passes, plate heat exchanger	—
$N_r$	Number of tubes in a vertical row	—
$N_s$	Number of sealing strips	—
$N_j$	Number of tubes in a tube bundle	—
$N_w$	Number of tubes in window zone	—
$N_{wv}$	Number of restrictions for cross flow in window zone	—
$P$	Total pressure	$ML^{-1}T^{-2}$
$P_c$	Critical pressure	$ML^{-1}T^{-2}$
$P_d$	Stack draft	L
$\Delta P_c$	Pressure drop in cross flow zone <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_e$	Pressure drop in end zone <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_i$	Pressure drop for cross flow over ideal tube bank <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_p$	Pressure drop in a plate heat exchanger <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_{pt}$	Pressure loss through the ports in a plate heat exchanger <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_s$	Shell-side pressure drop <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_t$	Tube-side pressure drop <sup>(1)</sup>	$ML^{-1}T^{-2}$
$\Delta P_w$	Pressure drop in window zone <sup>(1)</sup>	$ML^{-1}T^{-2}$
$p'$	Atmospheric pressure	$ML^{-1}T^{-2}$
$p_i$	Fin pitch	L
$p_s$	Saturation vapour pressure	$ML^{-1}T^{-2}$
$p_t$	Tube pitch	L
$p'_t$	Vertical tube pitch	L
$p_w$	Saturation vapour pressure corresponding to wall temperature	$ML^{-1}T^{-2}$
$Q$	Heat transferred in unit time	$ML^2T^{-3}$
$Q_g$	Sensible-heat-transfer rate from gas phase	$ML^2T^{-3}$
$Q_t$	Total heat-transfer rate from gas phase	$ML^2T^{-3}$
$q$	Heat flux (heat-transfer rate per unit area)	$MT^{-3}$
$q'$	Uncorrected value of flux from Figure 12.59	$MT^{-3}$
$q_c$	Maximum (critical) flux for a single tube	$MT^{-3}$
$q_{cb}$	Maximum flux for a tube bundle	$MT^{-3}$
$q_r$	Radiant heat flux	$MT^{-3}$
$R$	Dimensionless temperature ratio defined by equation 12.6	—
$R_a$	Ratio of window area to total area	—
$R'_a$	Ratio of bundle cross-sectional area in window zone to total cross-sectional area of bundle	—
$R_w$	Ratio number of tubes in window zones to total number	—
$S$	Dimensionless temperature ratio defined by equation 12.7	—
$T$	Shell-side temperature	$\theta$
$T$	Temperature of surface	$\theta$
$T_a$	Ambient temperature	$\theta$
$T_g$	Temperature of combustion gases	$\theta$
$T_{ga}$	Average flue-gas temperature	$\theta$
$T_r$	Reduced temperature	—
$T_s$	Saturation temperature	$\theta$
$T_{sat}$	Saturation temperature	$\theta$
$T_t$	Tube surface temperature	$\theta$
$T_v$	Vapour (gas) temperature	$\theta$
$T_w$	Wall (surface) temperature	$\theta$
$T_1$	Shell-side inlet temperature	$\theta$
$T_2$	Shell-side exit temperature	$\theta$
$\Delta T$	Temperature difference	$\theta$
$\Delta T_{lm}$	Logarithmic mean temperature difference	$\theta$
$\Delta T_m$	Mean temperature difference in equation 12.1	$\theta$
$\Delta T_s$	Temperature change in vapour (gas) stream	$\theta$
$t$	Tube-side temperature	$\theta$
$t_c$	Local coolant temperature	$\theta$

$t_f$	Fin thickness	L
$t_1$	Tube-side inlet temperature	$\theta$
$t_2$	Tube-side exit temperature	$\theta$
$U$	Overall heat-transfer coefficient	$MT^{-3}\theta^{-1}$
$U'$	Uncorrected overall coefficient, equation 12.72	$MT^{-3}\theta^{-1}$
$U_c$	Corrected overall coefficient, equation 12.72	$MT^{-3}\theta^{-1}$
$U_o$	Overall heat-transfer coefficient based on tube outside area	$MT^{-3}\theta^{-1}$
$u$	Fluid velocity	$LT^{-1}$
$u_L$	Liquid velocity, equation 12.55	$LT^{-1}$
$u_p$	Fluid velocity in a plate heat exchanger	$LT^{-1}$
$u_{pt}$	Velocity through the ports of a plate heat exchanger	$LT^{-1}$
$u_p$	Velocity through channels of a plate heat exchanger	$LT^{-1}$
$u_s$	Shell-side fluid velocity	$LT^{-1}$
$u_t$	Tube-side fluid velocity	$LT^{-1}$
$u_v$	Vapour velocity, equation 12.55	$LT^{-1}$
$\hat{u}_v$	Maximum vapour velocity in kettle reboiler	$LT^{-1}$
$u_w$	Velocity in window zone	$LT^{-1}$
$u_z$	Geometric mean velocity	$LT^{-1}$
$W$	Mass flow-rate of fluid	$MT^{-1}$
$w$	Mass flow through the channels and ports in a plate heat exchanger	$MT^{-1}$
$W_c$	Total condensate mass flow-rate	$MT^{-1}$
$W_s$	Shell-side fluid mass flow-rate	$MT^{-1}$
$X_{tt}$	Lockhart-Martinelli two-phase flow parameter	—
$x$	Mass fraction of vapour	—
$Z$	Ratio of change in sensible heat of gas stream to change in total heat of gas stream (sensible + latent)	—
$\alpha$	Absorption efficiency factor	—
$\alpha$	Factor in equation 12.30	—
$\beta_L$	Factor in equation 12.31, for heat transfer	—
$\beta'_L$	Factor in equation 12.31, for pressure drop	—
$\theta_b$	Angle subtended by baffle chord	—
$\lambda$	Latent heat	$L^2T^{-2}$
$\mu$	Viscosity at bulk fluid temperature	$ML^{-1}T^{-1}$
$\mu_L$	Liquid viscosity	$ML^{-1}T^{-1}$
$\mu_v$	Vapour viscosity	$ML^{-1}T^{-1}$
$\mu_w$	Viscosity at wall temperature	$ML^{-1}T^{-1}$
$\rho$	Fluid density	$ML^{-3}$
$\rho_L$	Liquid density	$ML^{-3}$
$\rho_v$	Vapour density	$ML^{-3}$
$\sigma$	Stephen-Boltzman constant	$MT^{-3}\theta^{-4}$
$\sigma$	Surface tension	$MT^{-2}$
$\Gamma$	Tube loading	$ML^{-1}T^{-1}$
$\Gamma_h$	Condensate loading on a horizontal tube	$ML^{-1}T^{-1}$
$\Gamma_v$	Condensate loading on a vertical tube	$ML^{-1}T^{-1}$
<i>Dimensionless numbers</i>		
Nu	Nusselt number	
Pr	Prandtl number	
Pr <sub>c</sub>	Prandtl number for condensate film	
Re	Reynolds number	
Re <sub>c</sub>	Reynolds number for condensate film	
Re <sub>L</sub>	Reynolds number for liquid phase	
St	Stanton number	

(1) *Note:* in Volumes 1 and 2 this symbol is used for pressure difference, and pressure drop (negative pressure gradient) indicated by a minus sign. In this chapter, as the symbol is only used for pressure drop, the minus sign has been omitted for convenience.

## 12.21. PROBLEMS

- 12.1** A solution of sodium hydroxide leaves a dissolver at 80°C and is to be cooled to 40°C, using cooling water. The maximum flow-rate of the solution will be 8000 kg/h. The maximum inlet temperature of the cooling water will be 20°C and the temperature rise is limited to 20°C.

Design a double-pipe exchanger for this duty, using standard carbon steel pipe and fittings. Use pipe of 50 mm inside diameter, 55 mm outside diameter for the inner pipe, and 75 mm inside diameter pipe for the outer. Make each section 5 m long. The physical properties of the caustic solution are:

temperature, °C	40	80
specific heat, kJkg <sup>-1</sup> °C <sup>-1</sup>	3.84	3.85
density, kg/m <sup>3</sup>	992.2	971.8
thermal conductivity, Wm <sup>-1</sup> °C <sup>-1</sup>	0.63	0.67
viscosity, mN m <sup>-2</sup> s	1.40	0.43

- 12.2.** A double-pipe heat exchanger is to be used to heat 6000 kg/h of 22 mol per cent hydrochloric acid. The exchanger will be constructed from karbate (impervious carbon) and steel tubing. The acid will flow through the inner, karbate, tube and saturated steam at 100°C will be used for heating. The tube dimensions will be: karbate tube inside diameter 50 mm, outside diameter 60 mm; steel tube inside diameter 100 mm. The exchanger will be constructed in sections, with an effective length of 3 m each.

How many sections will be needed to heat the acid from 15 to 65°C?

Physical properties of 22 % HCl at 40°C: specific heat 4.93 kJkg<sup>-1</sup>°C<sup>-1</sup>, thermal conductivity 0.39 Wm<sup>-1</sup>°C<sup>-1</sup>, density 866 kg/m<sup>3</sup>.

Viscosity:	temperature	20	30	40	50	60	70°C
	mN m <sup>-2</sup> s	0.68	0.55	0.44	0.36	0.33	0.30

Karbonate thermal conductivity 480 Wm<sup>-1</sup>°C<sup>-1</sup>.

- 12.3.** In a food processing plant there is a requirement to heat 50,000 kg/h of towns water from 10 to 70°C. Steam at 2.7 bar is available for heating the water. An existing heat exchanger is available, with the following specification:

Shell inside diameter 337 mm, E type.

Baffles 25 per cent cut, set at a spacing of 106 mm.

Tubes 15 mm inside diameter, 19 mm outside diameter, 4094 mm long.

Tube pitch 24 mm, triangular.

Number of tubes 124, arranged in a single pass.

Would this exchanger be suitable for the specified duty?

- 12.4.** Design a shell and tube exchanger to heat 50,000 kg/h of liquid ethanol from 20°C to 80°C. Steam at 1.5 bar is available for heating. Assign the ethanol to the tube-side. The total pressure drop must not exceed 0.7 bar for the alcohol stream. Plant practice requires the use of carbon steel tubes, 25 mm inside diameter, 29 mm outside diameter, 4 m long.

Set out your design on a data sheet and make a rough sketch of the heat exchanger. The physical properties of ethanol can be readily found in the literature.

- 12.5.** 4500 kg/h of ammonia vapour at 6.7 bara pressure is to be cooled from 120°C to 40°C, using cooling water. The maximum supply temperature of the cooling water available is 30°C, and the outlet temperature is to be restricted to 40°C. The pressure drops over the exchanger must not exceed 0.5 bar for the ammonia stream and 1.5 bar for the cooling water.

A contractor has proposed using a shell and tube exchanger with the following specification for this duty.

Shell: E-type, inside diameter 590 mm.

Baffles: 25 per cent cut, 300 mm spacing.

Tubes: carbon steel, 15 mm inside diameter, 19 mm outside diameter, 2400 mm long, number 360.

Tube arrangement: 8 passes, triangular tube pitch, pitch 23.75 mm.

Nozzles: shell 150 mm inside diameter, tube headers 75 mm inside diameter.

It is proposed to put the cooling water through the tubes.

Is the proposed design suitable for the duty?

Physical properties of ammonia at the mean temperature of 80°C:

specific heat 2.418 kJkg<sup>-1</sup>C<sup>-1</sup>, thermal conductivity 0.0317 Wm<sup>-1</sup> C<sup>-1</sup>, density 4.03 kg/m<sup>3</sup>, viscosity 1.21 × 10<sup>-5</sup> N m<sup>-2</sup>s.

- 12.6.** A vaporiser is required to evaporate 10,000 kg/h of a process fluid, at 6 bar. The liquid is fed to the vaporiser at 20°C.

The plant has a spare kettle reboiler available with the following specification.

U-tube bundle, 50 tubes, mean length 4.8 m, end to end.

Carbon steel tubes, inside diameter 25 mm, outside diameter 30 mm, square pitch 45 mm.

Steam at 1.7 bara will be used for heating.

Check if this reboiler would be suitable for the duty specified. Only check the thermal design. You may take it that the shell will handle the vapour rate.

Take the physical properties of the process fluid as:

liquid: density 535 kg/m<sup>3</sup>, specific heat 2.6 kJkg<sup>-1</sup>C<sup>-1</sup>, thermal conductivity 0.094 Wm<sup>-1</sup>C<sup>-1</sup>, viscosity 0.12 mN m<sup>-2</sup>s, surface tension 0.85 N/m, heat of vaporisation 322 kJ/kg.

Vapour density 14.4 kg/m<sup>3</sup>.

Vapour pressure:

temperature°C	50	60	70	80	90	100	110	120
pressure bar	5.0	6.4	8.1	10.1	12.5	15.3	18.5	20.1

- 12.7.** A condenser is required to condense n-propanol vapour leaving the top of a distillation column. The n-propanol is essentially pure, and is a saturated vapour at a pressure of 2.1 bara. The condensate needs to be sub-cooled to 45°C.

Design a horizontal shell and tube condenser capable of handling a vapour rate of 30,000 kg/h. Cooling water is available at 30°C and the temperature rise is to be limited to 30°C. The pressure drop on the vapour stream is to be less than 50 kN/m<sup>2</sup>, and on the water stream less than 70 kN/m<sup>2</sup>. The preferred tube size is 16 mm inside diameter, 19 mm outside diameter, and 2.5 m long.



Take the saturation temperature of n-propanol at 2.1 bar as 118°C. The other physical properties required can be found in the literature, or estimated.

- 12.8.** Design a vertical shell and tube condenser for the duty given in question 12.7. Use the same preferred tube size.
- 12.9.** In the manufacture of methyl ethyl ketone (MEK) from 2-butanol, the reactor products are pre-cooled and then partially condensed in a shell and tube exchanger. A typical analysis of the stream entering the condenser is, mol fractions: MEK 0.47, unreacted alcohol 0.06, hydrogen 0.47. Only 85 per cent of the MEK and alcohol are condensed. The hydrogen is non-condensable. The vapours enter the condenser at 125°C and the condensate and uncondensed material leave at 27°C. The condenser pressure is maintained at 1.1 bara. Make a preliminary design of this condenser, for a feed rate of 1500 kg/h. Chilled water will be used as the coolant, at an inlet temperature of 10°C and allowable temperature rise of 30°C. Any of the physical properties of the components not available in Appendix C, or the general literature, should be estimated.
- 12.10.** A vertical thermosyphon reboiler is required for a column. The liquid at the base of the column is essentially pure n-butane. A vapour rate of 5 kg/s is required. The pressure at the base of the column is 20.9 bar. Saturated steam at 5 bar will be used for heating. Estimate the number of 25 mm outside diameter, 22 mm inside diameter, 4 m long, tubes needed. At 20.9 bar the saturation temperature of n-butane is 117°C and the heat of vaporisation 828 kJ/kg.
- 12.11.** An immersed bundle vaporiser is to be used to supply chlorine vapour to a chlorination reactor, at a rate of 10,000 kg/h. The chlorine vapour is required at 5 bar pressure. The minimum temperature of the chlorine feed will be 10°C. Hot water at 50°C is available for heating. The pressure drop on the water side must not exceed 0.8 bar. Design a vaporiser for this duty. Use stainless steel U-tubes, 6 m long, 21 mm inside diameter, 25 mm outside diameter, on a square pitch of 40 mm. The physical properties of chlorine at 5 bar are: saturation temperature 10°C, heat of vaporisation 260 kJ/kg, specific heat 0.99 kJkg<sup>-1</sup>°C<sup>-1</sup>, thermal conductivity 0.13 Wm<sup>-1</sup>°C<sup>-1</sup>, density 1440 kg/m<sup>3</sup>, viscosity 0.3 mN m<sup>-2</sup>s, surface tension 0.013 N/m, vapour density 16.3 kg/m<sup>3</sup>. The vapour pressure can be estimated from the equation:

$$\ln(P) = 9.34 - 1978/(T + 246); \quad P \text{ bar, } T^\circ\text{C}$$

- 12.12.** There is a requirement to cool 200,000 kg/h of a dilute solution of potassium carbonate from 70 to 30°C. Cooling water will be used for cooling, with inlet and outlet temperatures of 20 and 60°C. A gasketed-plate heat exchanger is available with the following specification:  
Number of plates 329.  
Effective plate dimensions: length 1.5 m, width 0.5 m, thickness 0.75 mm.

Channel width 3 mm.

Flow arrangement two pass: two pass.

Port diameters 150 mm.

Check if this exchanger is likely to be suitable for the thermal duty required, and estimate the pressure drop for each stream.

Take the physical properties of the dilute potassium carbonate solution to be the same as those for water.

# *Mechanical Design of Process Equipment*

## **13.1. INTRODUCTION**

This chapter covers those aspects of the mechanical design of chemical plant that are of particular interest to chemical engineers. The main topic considered is the design of pressure vessels. The design of storage tanks, centrifuges and heat-exchanger tube sheets are also discussed briefly.

The chemical engineer will not usually be called on to undertake the detailed mechanical design of a pressure vessel. Vessel design is a specialised subject, and will be carried out by mechanical engineers who are conversant with the current design codes and practices, and methods of stress analysis. However, the chemical engineer will be responsible for developing and specifying the basic design information for a particular vessel, and needs to have a general appreciation of pressure vessel design to work effectively with the specialist designer.

The basic data needed by the specialist designer will be:

1. Vessel function.
2. Process materials and services.
3. Operating and design temperature and pressure.
4. Materials of construction.
5. Vessel dimensions and orientation.
6. Type of vessel heads to be used.
7. Openings and connections required.
8. Specification of heating and cooling jackets or coils.
9. Type of agitator.
10. Specification of internal fittings.

A data sheet for pressure vessel design is given in Appendix G.

There is no strict definition of what constitutes a pressure vessel, but it is generally accepted that any closed vessel over 150 mm diameter subject to a pressure difference of more than 0.5 bar should be designed as a pressure vessel.

It is not possible to give a completely comprehensive account of vessel design in one chapter. The design methods and data given should be sufficient for the preliminary design of conventional vessels. Sufficient for the chemical engineer to check the feasibility of a proposed equipment design; to estimate the vessel cost for an economic analysis; and to determine the vessel's general proportions and weight for plant layout purposes. For a more detailed account of pressure vessel design the reader should refer to the books

by Singh and Soler (1992), Escoe (1994) and Moss (1987). Other useful books on the mechanical design of process equipment are listed in the bibliography at the end of this chapter.

An elementary understanding of the principles of the “Strength of Materials” (Mechanics of Solids) will be needed to follow this chapter. Readers who are not familiar with the subject should consult one of the many textbooks available; such as those by Case *et al.* (1999), Mott, R. L. (2001), Seed (2001) and Gere and Timoshenko (2000).

### 13.1.1. Classification of pressure vessels

For the purposes of design and analysis, pressure vessels are sub-divided into two classes depending on the ratio of the wall thickness to vessel diameter: thin-walled vessels, with a thickness ratio of less than 1 : 10; and thick-walled above this ratio.

The principal stresses (see Section 13.3.1) acting at a point in the wall of a vessel, due to a pressure load, are shown in Figure 13.1. If the wall is thin, the radial stress  $\sigma_3$  will be small and can be neglected in comparison with the other stresses, and the longitudinal and circumferential stresses  $\sigma_1$  and  $\sigma_2$  can be taken as constant over the wall thickness. In a thick wall, the magnitude of the radial stress will be significant, and the circumferential stress will vary across the wall. The majority of the vessels used in the chemical and allied industries are classified as thin-walled vessels. Thick-walled vessels are used for high pressures, and are discussed in Section 13.15.

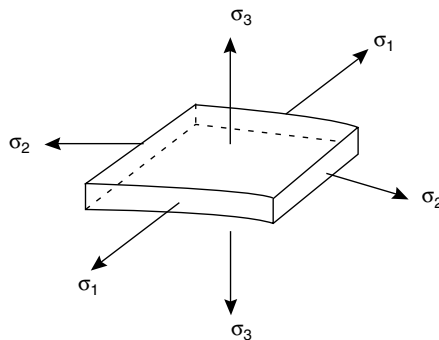


Figure 13.1. Principal stresses in pressure-vessel wall

## 13.2. PRESSURE VESSEL CODES AND STANDARDS

In all the major industrialised countries the design and fabrication of thin-walled pressure vessels is covered by national standards and codes of practice. In most countries the standards and codes are legally enforceable.

In the United Kingdom all conventional pressure vessels for use in the chemical and allied industries will invariably be designed and fabricated according to the British Standard PD 5500 or the European Standard EN 13445; or an equivalent code such as the American Society of Mechanical Engineers code Section VIII (the ASME code). The codes and standards cover design, materials of construction, fabrication (manufacture and

workmanship), and inspection and testing. They form a basis of agreement between the manufacturer and customer, and the customer's insurance company.

In the European Union the design, manufacture and use of pressure systems is also covered by the Pressure Equipment Directive (Council Directive 97/23/EC) whose use became mandatory in May 2002.

The current (2003) edition of PD 5500 covers vessels fabricated in carbon and alloy steels, and aluminium. The design of vessels constructed from reinforced plastics is covered by BS 4994. The ASME code covers steels, non-ferrous metals, and fibre-reinforced plastics.

Where national codes are not available, the British, European or American codes would be used.

Information and guidance on the pressure vessel codes can be found on the Internet; [www.bsi-global.com](http://www.bsi-global.com).

A comprehensive review of the ASME code is given by Chuse and Carson (1992) and Yokell (1986); see also Perry *et al.* (1997).

The national codes and standards dictate the minimum requirements, and give general guidance for design and construction; any extension beyond the minimum code requirement will be determined by agreement between the manufacturer and customer.

The codes and standards are drawn up by committees of engineers experienced in vessel design and manufacturing techniques, and are a blend of theory, experiment and experience. They are periodically reviewed, and revisions issued to keep abreast of developments in design, stress analysis, fabrication and testing. The latest version of the appropriate national code or standard should always be consulted before undertaking the design of any pressure vessel.

Computer programs to aid in the design of vessels to PD 5500 and the ASME code are available from several commercial organisations and can be found by making a search of the World Wide Web.

### 13.3. FUNDAMENTAL PRINCIPLES AND EQUATIONS

This section has been included to provide a basic understanding of the fundamental principles that underlie the design equations given in the sections that follow. The derivation of the equations is given in outline only. A full discussion of the topics covered can be found in any text on the "Strength of Materials" (Mechanics of Solids).

#### 13.3.1. Principal stresses

The state of stress at a point in a structural member under a complex system of loading is described by the magnitude and direction of the principal stresses. The principal stresses are the maximum values of the normal stresses at the point; which act on planes on which the shear stress is zero. In a two-dimensional stress system, Figure 13.2, the principal stresses at any point are related to the normal stresses in the  $x$  and  $y$  directions  $\sigma_x$  and  $\sigma_y$  and the shear stress  $\tau_{xy}$  at the point by the following equation:

$$\text{Principal stresses, } \sigma_1, \sigma_2 = \frac{1}{2}(\sigma_y + \sigma_x) \pm \frac{1}{2}\sqrt{[(\sigma_y - \sigma_x)^2 + 4\tau_{xy}^2]} \quad (13.1)$$

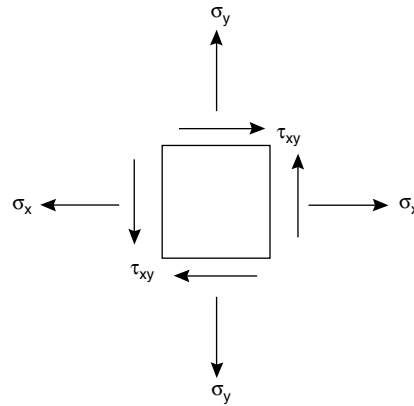


Figure 13.2. Two-dimensional stress system

The maximum shear stress at the point is equal to half the algebraic difference between the principal stresses:

$$\text{Maximum shear stress} = \frac{1}{2}(\sigma_1 - \sigma_2) \quad (13.2)$$

Compressive stresses are conventionally taken as negative; tensile as positive.

### 13.3.2. Theories of failure

The failure of a simple structural element under unidirectional stress (tensile or compressive) is easy to relate to the tensile strength of the material, as determined in a standard tensile test, but for components subjected to combined stresses (normal and shear stress) the position is not so simple, and several theories of failure have been proposed. The three theories most commonly used are described below:

*Maximum principal stress theory:* which postulates that a member will fail when one of the principal stresses reaches the failure value in simple tension,  $\sigma'_e$ . The failure point in a simple tension is taken as the yield-point stress, or the tensile strength of the material, divided by a suitable factor of safety.

*Maximum shear stress theory:* which postulates that failure will occur in a complex stress system when the maximum shear stress reaches the value of the shear stress at failure in simple tension.

For a system of combined stresses there are three shear stresses maxima:

$$\tau_1 = \frac{\sigma_1 - \sigma_2}{2} \quad (13.3a)$$

$$\tau_2 = \frac{\sigma_2 - \sigma_3}{2} \quad (13.3b)$$

$$\tau_3 = \frac{\sigma_3 - \sigma_1}{2} \quad (13.3c)$$

In the tensile test, 
$$\tau_e = \frac{\sigma'_e}{2} \quad (13.4)$$

The maximum shear stress will depend on the sign of the principal stresses as well as their magnitude, and in a two-dimensional stress system, such as that in the wall of a thin-walled pressure vessel, the maximum value of the shear stress may be that given by putting  $\sigma_3 = 0$  in equations 13.3*b* and *c*.

The maximum shear stress theory is often called Tresca's, or Guest's, theory.

*Maximum strain energy theory*: which postulates that failure will occur in a complex stress system when the total strain energy per unit volume reaches the value at which failure occurs in simple tension.

The maximum shear-stress theory has been found to be suitable for predicting the failure of ductile materials under complex loading and is the criterion normally used in the pressure-vessel design.

### 13.3.3. Elastic stability

Under certain loading conditions failure of a structure can occur not through gross yielding or plastic failure, but by buckling, or wrinkling. Buckling results in a gross and sudden change of shape of the structure; unlike failure by plastic yielding, where the structure retains the same basic shape. This mode of failure will occur when the structure is not elastically stable: when it lacks sufficient stiffness, or rigidity, to withstand the load. The stiffness of a structural member is dependent not on the basic strength of the material but on its elastic properties ( $E$  and  $\nu$ ) and the cross-sectional shape of the member.

The classic example of failure due to elastic instability is the buckling of tall thin columns (struts), which is described in any elementary text on the "Strength of Materials".

For a structure that is likely to fail by buckling there will be a certain critical value of load below which the structure is stable; if this value is exceeded catastrophic failure through buckling can occur.

The walls of pressure vessels are usually relatively thin compared with the other dimensions and can fail by buckling under compressive loads.

Elastic buckling is the decisive criterion in the design of thin-walled vessels under external pressure.

### 13.3.4. Membrane stresses in shells of revolution

A shell of revolution is the form swept out by a line or curve rotated about an axis. (A solid of revolution is formed by rotating an area about an axis.) Most process vessels are made up from shells of revolution: cylindrical and conical sections; and hemispherical, ellipsoidal and torispherical heads; Figure 13.3.

The walls of thin vessels can be considered to be "membranes"; supporting loads without significant bending or shear stresses; similar to the walls of a balloon.

The analysis of the membrane stresses induced in shells of revolution by internal pressure gives a basis for determining the minimum wall thickness required for vessel shells. The actual thickness required will also depend on the stresses arising from the other loads to which the vessel is subjected.

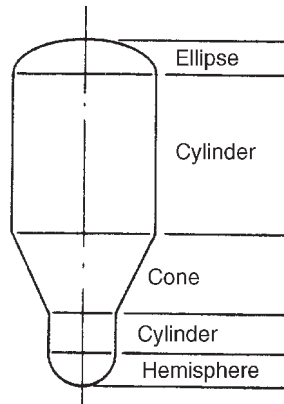


Figure 13.3. Typical vessel shapes

Consider the shell of revolution of general shape shown in Figure 13.4, under a loading that is rotationally symmetric; that is, the load per unit area (pressure) on the shell is constant round the circumference, but not necessarily the same from top to bottom.

Let  $P$  = pressure,

$t$  = thickness of shell,

$\sigma_1$  = the meridional (longitudinal) stress, the stress acting along a meridian,

$\sigma_2$  = the circumferential or tangential stress, the stress acting along parallel circles (often called the hoop stress),

$r_1$  = the meridional radius of curvature,

$r_2$  = circumferential radius of curvature.

*Note:* the vessel has a double curvature; the values of  $r_1$  and  $r_2$  are determined by the shape.

Consider the forces acting on the element defined by the points  $a, b, c, d$ . Then the normal component (component acting at right angles to the surface) of the pressure force on the element

$$= P \left[ 2r_1 \sin \left( \frac{d\theta_1}{2} \right) \right] \left[ 2r_2 \sin \left( \frac{d\theta_2}{2} \right) \right]$$

This force is resisted by the normal component of the forces associated with the membrane stresses in the walls of the vessel (given by, force = stress  $\times$  area)

$$= 2\sigma_2 t dS_1 \sin \left( \frac{d\theta_2}{2} \right) + 2\sigma_1 t dS_2 \sin \left( \frac{d\theta_1}{2} \right)$$

Equating these forces and simplifying, and noting that in the limit  $d\theta/2 \rightarrow dS/2r$ , and  $\sin d\theta \rightarrow d\theta$ , gives:

$$\frac{\sigma_1}{r_1} + \frac{\sigma_2}{r_2} = \frac{P}{t} \quad (13.5)$$



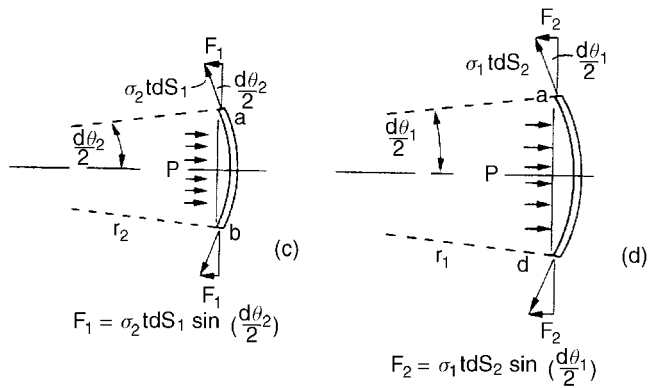
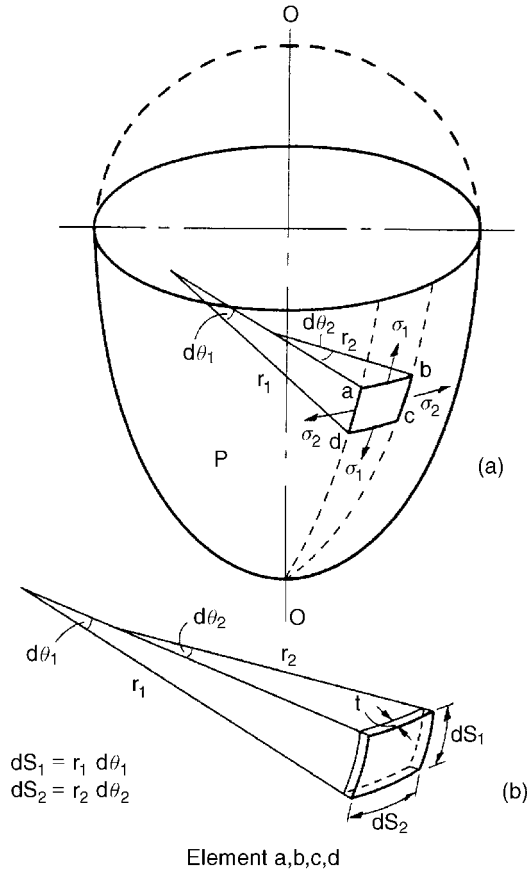


Figure 13.4(a)(b). Stress in a shell of revolution (c)(d). Forces acting on sides of element *abcd*

An expression for the meridional stress  $\sigma_1$  can be obtained by considering the equilibrium of the forces acting about any circumferential line, Figure 13.5. The vertical component of the pressure force

$$= P\pi(r_2 \sin \theta)^2$$

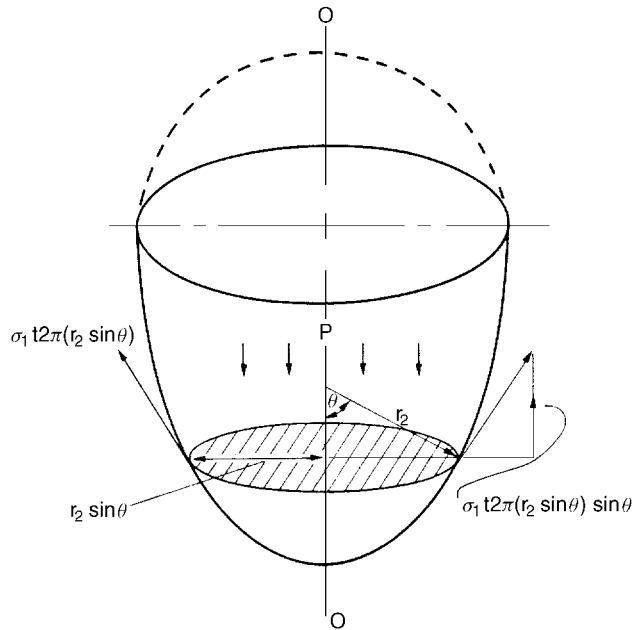


Figure 13.5. Meridional stress, force acting at a horizontal plane

This is balanced by the vertical component of the force due to the meridional stress acting in the ring of the wall of the vessel

$$= 2\sigma_1 t \pi (r_2 \sin \theta) \sin \theta$$

Equating these forces gives:

$$\sigma_1 = \frac{Pr_2}{2t} \quad (13.6)$$

Equations 13.5 and 13.6 are completely general for any shell of revolution.

### **Cylinder (Figure 13.6a)**

A cylinder is swept out by the rotation of a line parallel to the axis of revolution, so:

$$r_1 = \infty$$

$$r_2 = \frac{D}{2}$$

where  $D$  is the cylinder diameter.

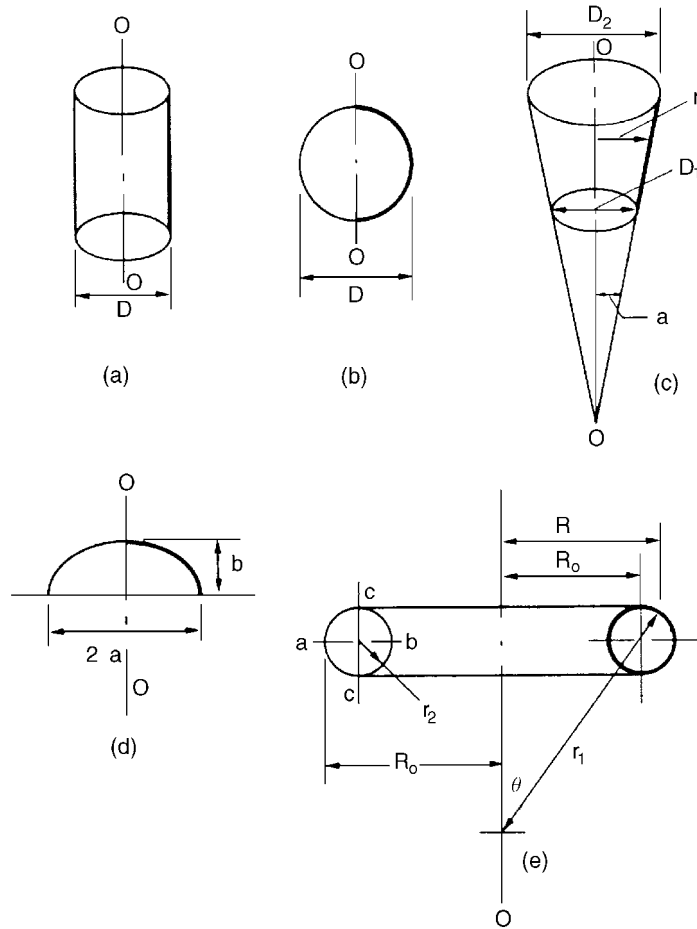


Figure 13.6. Shells of revolution

Substitution in equations 13.5 and 13.6 gives:

$$\sigma_2 = \frac{PD}{2t} \quad (13.7)$$

$$\sigma_1 = \frac{PD}{4t} \quad (13.8)$$

### **Sphere (Figure 13.6b)**

$$r_1 = r_2 = \frac{D}{2}$$

hence:

$$\sigma_1 = \sigma_2 = \frac{PD}{4t} \quad (13.9)$$

**Cone (Figure 13.6c)**

A cone is swept out by a straight line inclined at an angle  $\alpha$  to the axis.

$$r_1 = \infty$$

$$r_2 = \frac{r}{\cos \alpha}$$

substitution in equations 13.5 and 13.6 gives:

$$\sigma_2 = \frac{Pr}{t \cos \alpha} \quad (13.10)$$

$$\sigma_1 = \frac{Pr}{2t \cos \alpha} \quad (13.11)$$

The maximum values will occur at  $r = D_2/2$ .

**Ellipsoid (Figure 13.6d)**

For an ellipse with major axis  $2a$  and minor axis  $2b$ , it can be shown that (see any standard geometry text):

$$r_1 = \frac{r_2^3 b^2}{a^4}$$

From equations 13.5 and 13.6

$$\sigma_1 = \frac{Pr_2}{2t} \quad (\text{equation 13.6})$$

$$\sigma_2 = \frac{P}{t} \left[ r_2 - \frac{r_2^2}{2r_1} \right] \quad (13.12)$$

At the crown (top)

$$r_1 = r_2 = \frac{a^2}{b}$$

$$\sigma_1 = \sigma_2 = \frac{Pa^2}{2tb} \quad (13.13)$$

At the equator (bottom)  $r_2 = a$ , so  $r_1 = b^2/a$

so

$$\sigma_1 = \frac{Pa}{2t} \quad (13.13)$$

$$\sigma_2 = \frac{P}{t} \left[ a - \frac{a^2}{2b^2/a} \right] = \frac{Pa}{t} \left[ 1 - \frac{1}{2} \frac{a^2}{b^2} \right] \quad (13.14)$$

It should be noted that if  $\frac{1}{2}(a/b)^2 > 1$ ,  $\sigma_2$  will be negative (compressive) and the shell could fail by buckling. This consideration places a limit on the practical proportions of ellipsoidal heads.

**Torus (Figure 13.6e)**

A torus is formed by rotating a circle, radius  $r_2$ , about an axis.

$$\sigma_1 = \frac{Pr_2}{2t} \quad \text{(equation 13.6)}$$

$$r_1 = \frac{R}{\sin \theta} = \frac{R_0 + r_2 \sin \theta}{\sin \theta}$$

and

$$\sigma_2 = \frac{Pr_2}{t} \left[ 1 - \frac{r_2 \sin \theta}{2(R_0 + r_2 \sin \theta)} \right] \quad (13.15)$$

On the centre line of the torus, point  $c$ ,  $\theta = 0$  and

$$\sigma_2 = \frac{Pr_2}{t} \quad (13.16)$$

At the outer edge, point  $a$ ,  $\theta = \pi/2$ ,  $\sin \theta = 1$  and

$$\sigma_2 = \frac{Pr_2}{2t} \left[ \frac{2R_0 + r_2}{R_0 + r_2} \right] \quad (13.17)$$

the minimum value.

At the inner edge, point  $b$ ,  $\theta = 3\pi/2$ ,  $\sin \theta = -1$  and

$$\sigma_2 = \frac{Pr_2}{2t} \left[ \frac{2R_0 - r_2}{R_0 - r_2} \right] \quad (13.18)$$

the maximum value.

So  $\sigma_2$  varies from a maximum at the inner edge to a minimum at the outer edge.

**Torispherical heads**

A torispherical shape, which is often used as the end closure of cylindrical vessels, is formed from part of a torus and part of a sphere, Figure 13.7. The shape is close to that of an ellipse but is easier and cheaper to fabricate.

In Figure 13.7  $R_k$  is the knuckle radius (the radius of the torus) and  $R_c$  the crown radius (the radius of the sphere). For the spherical portion:

$$\sigma_1 = \sigma_2 = \frac{PR_c}{2t} \quad (13.19)$$

For the torus:

$$\sigma_1 = \frac{PR_k}{2t} \quad (13.20)$$

$\sigma_2$  depends on the location, and is a function of  $R_c$  and  $R_k$ ; it can be calculated from equations 13.15 and 13.9.

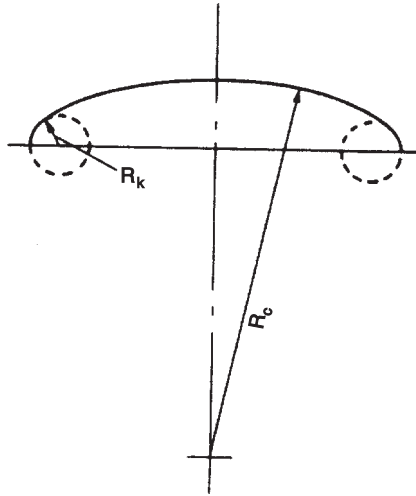


Figure 13.7. Torisphere

The ratio of the knuckle radius to crown radius should be made not less than 6/100 to avoid buckling. The stress will be higher in the torus section than the spherical section.

### 13.3.5. Flat plates

Flat plates are used as covers for manholes, as blind flanges, and for the ends of small diameter and low pressure vessels.

For a uniformly loaded circular plate supported at its edges, the slope  $\phi$  at any radius  $x$  is given by:

$$\phi = -\frac{dw}{dx} = -\frac{1}{\mathbf{D}} \frac{Px^3}{16} + \frac{C_1x}{2} + \frac{C_2}{x} \quad (13.21)$$

(The derivation of this equation can be found in any text on the strength of materials.)

Integration gives the deflection  $w$ :

$$w = \frac{Px^4}{64\mathbf{D}} - C_1 \frac{x^2}{4} - C_2 \ln x + C_3 \quad (13.22)$$

where  $P$  = intensity of loading (pressure),

$x$  = radial distance to point of interest,

$\mathbf{D}$  = flexural rigidity of plate =  $(Et^3)/(12(1 - \nu^2))$ ,

$t$  = plate thickness,

$\nu$  = Poisson's ratio for the material,

$E$  = modulus of elasticity of the material (Young's modulus).

$C_1$ ,  $C_2$ ,  $C_3$  are constants of integration which can be obtained from the boundary conditions at the edge of the plate.

Two limiting situations are possible:

1. When the edge of the plate is rigidly clamped, not free to rotate; which corresponds to a heavy flange, or a strong joint.
2. When the edge is free to rotate (simply supported); corresponding to a weak joint, or light flange.

### 1. Clamped edges (Figure 13.8a)

The edge (boundary) conditions are:

$$\phi = 0 \text{ at } x = 0$$

$$\phi = 0 \text{ at } x = a$$

$$w = 0 \text{ at } x = a$$

where  $a$  is the radius of the plate.

Which gives:

$$C_2 = 0, \quad C_1 = \frac{Pa^2}{8\mathbf{D}}, \quad \text{and} \quad C_3 = \frac{Pa^4}{64\mathbf{D}}$$

hence

$$\phi = \frac{Px}{16\mathbf{D}}(a^2 - x^2) \quad (13.23)$$

and

$$w = \frac{P}{64\mathbf{D}}(x^2 - a^2)^2 \quad (13.24)$$

The maximum deflection will occur at the centre of the plate at  $x = 0$

$$\hat{w} = \frac{Pa^4}{64\mathbf{D}} \quad (13.25)$$

The bending moments per unit length due to the pressure load are related to the slope and deflection by:

$$M_1 = \mathbf{D} \left[ \frac{d\phi}{dx} + \nu \frac{\phi}{x} \right] \quad (13.26)$$

$$M_2 = \mathbf{D} \left[ \frac{\phi}{x} + \nu \frac{d\phi}{dx} \right] \quad (13.27)$$

Where  $M_1$  is the moment acting along cylindrical sections, and  $M_2$  that acting along diametrical sections.

Substituting for  $\phi$  and  $d\phi/dx$  in equations 13.26 and 13.27 gives:

$$M_1 = \frac{P}{16}[a^2(1 + \nu) - x^2(3 + \nu)] \quad (13.28)$$

$$M_2 = \frac{P}{16}[a^2(1 + \nu) - x^2(1 + 3\nu)] \quad (13.29)$$

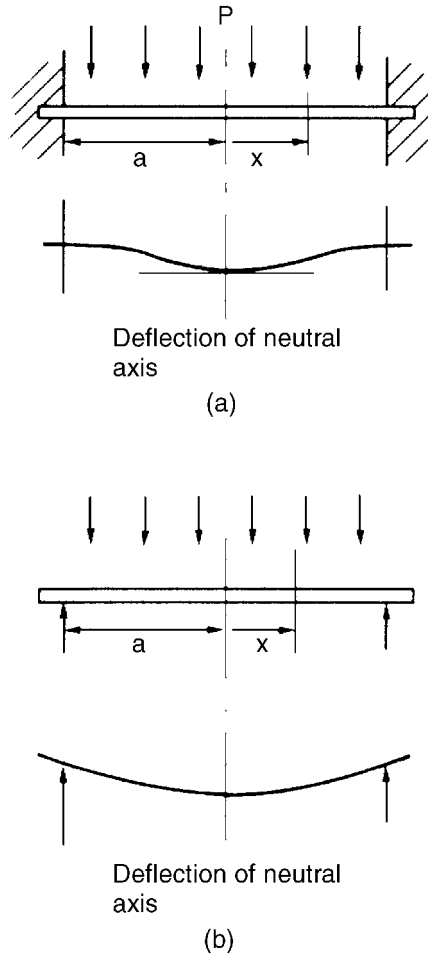


Figure 13.8. Flat circular plates (a) Clamped edges (b) Simply supported

The maximum values will occur at the edge of the plate,  $x = a$ .

$$\hat{M}_1 = -\frac{Pa^2}{8}, \quad \hat{M}_2 = -\nu \frac{Pa^2}{8}$$

The bending stress is given by:

$$\sigma_b = \frac{M_1}{I'} \times \frac{t}{2}$$

where  $I' =$  second moment of area per unit length  $= t^3/12$ , hence

$$\hat{\sigma}_b = \frac{6\hat{M}_1}{t^2} = \frac{3}{4} \frac{Pa^2}{t^2} \quad (13.30)$$



## 2. Simply supported plate (Figure 13.8b)

The edge (boundary) conditions are:

$$\phi = 0 \text{ at } x = 0$$

$$w = 0 \text{ at } x = a$$

$$M_1 = 0 \text{ at } x = a \text{ (free to rotate)}$$

which gives  $C_2$  and  $C_3 = 0$ .

Hence

$$\phi = -\frac{1}{D} \frac{Px^3}{16} + \frac{C_1 x}{2}$$

and

$$\frac{d\phi}{dx} = -\frac{1}{D} \left[ \frac{3Px^2}{16} \right] + \frac{C_1}{2}$$

Substituting these values in equation 13.26, and equating to zero at  $x = a$ , gives:

$$C_1 = \frac{Pa^2 (3 + \nu)}{8D (1 + \nu)}$$

and hence

$$M_1 = \frac{P}{16} (3 + \nu) (a^2 - x^2) \quad (13.31)$$

The maximum bending moment will occur at the centre, where  $M_1 = M_2$

$$\hat{M}_1 = \hat{M}_2 = \frac{P(3 + \nu)a^2}{16} \quad (13.32)$$

$$\hat{\sigma}_b = \frac{6\hat{M}_1}{t^2} = \frac{3}{8} (3 + \nu) \frac{Pa^2}{t^2} \quad (13.33)$$

### General equation for flat plates

A general equation for the thickness of a flat plate required to resist a given pressure load can be written in the form:

$$t = CD \sqrt{\frac{P}{f}} \quad (13.34)$$

where  $f$  = the maximum allowable stress (the design stress),

$D$  = the effective plate diameter,

$C$  = a constant, which depends on the edge support.

The limiting value of  $C$  can be obtained from equations 13.30 and 13.33. Taking Poisson's ratio as 0.3, a typical value for steels, then if the edge can be taken as completely rigid  $C = 0.43$ , and if it is essentially free to rotate  $C = 0.56$ .

### 13.3.6. Dilation of vessels

Under internal pressure a vessel will expand slightly. The radial growth can be calculated from the elastic strain in the radial direction. The principal strains in a two-dimensional system are related to the principal stresses by:

$$\varepsilon_1 = \frac{1}{E}(\sigma_1 - \nu\sigma_2) \quad (13.35)$$

$$\varepsilon_2 = \frac{1}{E}(\sigma_2 - \nu\sigma_1) \quad (13.36)$$

The radial (diametrical strain) will be the same as the circumferential strain  $\varepsilon_2$ . For any shell of revolution the dilation can be found by substituting the appropriate expressions for the circumferential and meridional stresses in equation 13.36.

The diametrical dilation  $\Delta = D\varepsilon_1$ .

For a cylinder

$$\sigma_1 = \frac{PD}{4t}$$

$$\sigma_2 = \frac{PD}{2t}$$

substitution in equation 13.36 gives:

$$\Delta_c = \frac{PD^2}{4tE}(2 - \nu) \quad (13.37)$$

For a sphere (or hemisphere)

$$\sigma_1 = \sigma_2 = \frac{PD}{4t}$$

and

$$\Delta_s = \frac{PD^2}{4tE}(1 - \nu) \quad (13.38)$$

So for a cylinder closed by a hemispherical head of the same thickness the difference in dilation of the two sections, if they were free to expand separately, would be:

$$\Delta_c - \Delta_s = \frac{PD^2}{4tE}$$

### 13.3.7. Secondary stresses

In the stress analysis of pressure vessels and pressure vessel components stresses are classified as primary or secondary. Primary stresses can be defined as those stresses that are necessary to satisfy the conditions of static equilibrium. The membrane stresses induced by the applied pressure and the bending stresses due to wind loads are examples of primary stresses. Primary stresses are not self-limiting; if they exceed the yield point of the material, gross distortion, and in the extreme situation, failure of the vessel will occur.

Secondary stresses are those stresses that arise from the constraint of adjacent parts of the vessel. Secondary stresses are self-limiting; local yielding or slight distortion will satisfy the conditions causing the stress, and failure would not be expected to occur in one application of the loading. The “thermal stress” set up by the differential expansion of parts of the vessel, due to different temperatures or the use of different materials, is an example of a secondary stress. The discontinuity that occurs between the head and the cylindrical section of a vessel is a major source of secondary stress. If free, the dilation of the head would be different from that of the cylindrical section (see Section 13.3.6); they are constrained to the same dilation by the welded joint between the two parts. The induced bending moment and shear force due to the constraint give rise to secondary bending and shear stresses at the junction. The magnitude of these discontinuity stresses can be estimated by analogy with the behaviour of beams on elastic foundations; see Hetenyi (1958) and Harvey (1974). The estimation of the stresses arising from discontinuities is covered in the books by Bednar (1990), and Jawad and Farr (1989).

Other sources of secondary stresses are the constraints arising at flanges, supports, and the change of section due to reinforcement at a nozzle or opening (see Section 13.6).

Though secondary stresses do not affect the “bursting strength” of the vessel, they are an important consideration when the vessel is subject to repeated pressure loading. If local yielding has occurred, residual stress will remain when the pressure load is removed, and repeated pressure cycling can lead to fatigue failure.

## **13.4. GENERAL DESIGN CONSIDERATIONS: PRESSURE VESSELS**

### **13.4.1. Design pressure**

A vessel must be designed to withstand the maximum pressure to which it is likely to be subjected in operation.

For vessels under internal pressure, the design pressure is normally taken as the pressure at which the relief device is set. This will normally be 5 to 10 per cent above the normal working pressure, to avoid spurious operation during minor process upsets. When deciding the design pressure, the hydrostatic pressure in the base of the column should be added to the operating pressure, if significant.

Vessels subject to external pressure should be designed to resist the maximum differential pressure that is likely to occur in service. Vessels likely to be subjected to vacuum should be designed for a full negative pressure of 1 bar, unless fitted with an effective, and reliable, vacuum breaker.

### **13.4.2. Design temperature**

The strength of metals decreases with increasing temperature (see Chapter 7) so the maximum allowable design stress will depend on the material temperature. The design temperature at which the design stress is evaluated should be taken as the maximum working temperature of the material, with due allowance for any uncertainty involved in predicting vessel wall temperatures.

### 13.4.3. Materials

Pressure vessels are constructed from plain carbon steels, low and high alloy steels, other alloys, clad plate, and reinforced plastics.

Selection of a suitable material must take into account the suitability of the material for fabrication (particularly welding) as well as the compatibility of the material with the process environment.

The pressure vessel design codes and standards include lists of acceptable materials; in accordance with the appropriate material standards.

### 13.4.4. Design stress (nominal design strength)

For design purposes it is necessary to decide a value for the maximum allowable stress (nominal design strength) that can be accepted in the material of construction.

This is determined by applying a suitable “design stress factor” (factor of safety) to the maximum stress that the material could be expected to withstand without failure under standard test conditions. The design stress factor allows for any uncertainty in the design methods, the loading, the quality of the materials, and the workmanship.

For materials not subject to high temperatures the design stress is based on the yield stress (or proof stress), or the tensile strength (ultimate tensile stress) of the material at the design temperature.

For materials subject to conditions at which the creep is likely to be a consideration, the design stress is based on the creep characteristics of the material: the average stress to produce rupture after  $10^5$  hours, or the average stress to produce a 1 per cent strain after  $10^5$  hours, at the design temperature. Typical design stress factors for pressure components are shown in Table 13.1.

Table 13.1. Design stress factors

Property	Material		
	Carbon Carbon-manganese, low alloy steels	Austenitic stainless steels	Non-ferrous metals
Minimum yield stress or 0.2 per cent proof stress, at the design temperature	1.5	1.5	1.5
Minimum tensile strength, at room temperature	2.35	2.5	4.0
Mean stress to produce rupture at $10^5$ h at the design temperature	1.5	1.5	1.0

In the British Standard, PD 5500, the nominal design strengths (allowable design stresses), for use with the design methods given, are listed in the standard, for the range

of materials covered by the standard. The standard should be consulted for the principles and design stress factors used in determining the nominal design strengths.

Typical design stress values for some common materials are shown in Table 13.2. These may be used for preliminary designs. The standards and codes should be consulted for the values to be used for detailed vessel design.

Table 13.2. Typical design stresses for plate  
(The appropriate material standards should be consulted for particular grades and plate thicknesses)

Material	Tensile strength (N/mm <sup>2</sup> )	Design stress at temperature °C (N/mm <sup>2</sup> )									
		0 to 50	100	150	200	250	300	350	400	450	500
Carbon steel (semi-killed or silicon killed)	360	135	125	115	105	95	85	80	70		
Carbon-manganese steel (semi-killed or silicon killed)	460	180	170	150	140	130	115	105	100		
Carbon-molybdenum steel, 0.5 per cent Mo	450	180	170	145	140	130	120	110	110		
Low alloy steel (Ni, Cr, Mo, V)	550	240	240	240	240	240	235	230	220	190	170
Stainless steel 18Cr/8Ni unstabilised (304)	510	165	145	130	115	110	105	100	100	95	90
Stainless steel 18Cr/8Ni Ti stabilised (321)	540	165	150	140	135	130	130	125	120	120	115
Stainless steel 18Cr/8Ni Mo 2½ per cent (316)	520	175	150	135	120	115	110	105	105	100	95

### 13.4.5. Welded joint efficiency, and construction categories

The strength of a welded joint will depend on the type of joint and the quality of the welding.

The soundness of welds is checked by visual inspection and by non-destructive testing (radiography).

The possible lower strength of a welded joint compared with the virgin plate is usually allowed for in design by multiplying the allowable design stress for the material by a “welded joint factor”  $J$ . The value of the joint factor used in design will depend on the type of joint and amount of radiography required by the design code. Typical values are shown in Table 13.3. Taking the factor as 1.0 implies that the joint is equally as strong as the virgin plate; this is achieved by radiographing the complete weld length, and cutting out and remaking any defects. The use of lower joint factors in design, though saving costs on radiography, will result in a thicker, heavier, vessel, and the designer must balance any cost savings on inspection and fabrication against the increased cost of materials.

Table 13.3. Maximum allowable joint efficiency

Type of joint	Degree of radiography		
	100 per cent	spot	none
Double-welded butt or equivalent	1.0	0.85	0.7
Single-weld butt joint with bonding strips	0.9	0.80	0.65

The national codes and standards divide vessel construction into different categories, depending on the amount of non-destructive testing required. The higher categories require 100 per cent radiography of the welds, and allow the use of highest values for the weld-joint factors. The lower-quality categories require less radiography, but allow only lower joint-efficiency factors, and place restrictions on the plate thickness and type of materials that can be used. The highest category will invariably be specified for process-plant pressure vessels.

The standards should be consulted to determine the limitations and requirements of the construction categories specified. Welded joint efficiency factors are not used, as such, in the design equations given in BS PD 5500; instead limitations are placed on the values of the nominal design strength (allowable design stress) for materials in the lower construction category. The standard specifies three construction categories:

Category 1: the highest class, requires 100 per cent non-destructive testing (NDT) of the welds; and allows the use of all materials covered by the standard, with no restriction on the plate thickness.

Category 2: requires less non-destructive testing but places some limitations on the materials which can be used and the maximum plate thickness.

Category 3: the lowest class, requires only visual inspection of the welds, but is restricted to carbon and carbon-manganese steels, and austenitic stainless steel; and limits are placed on the plate thickness and the nominal design stress. For carbon and carbon-manganese steels the plate thickness is restricted to less than 13 mm and the design stress is about half that allowed for categories 1 and 2. For stainless steel the thickness is restricted to less than 25 mm and the allowable design stress is around 80 per cent of that for the other categories.

#### 13.4.6. Corrosion allowance

The “corrosion allowance” is the additional thickness of metal added to allow for material lost by corrosion and erosion, or scaling (see Chapter 7). The allowance to be used should be agreed between the customer and manufacturer. Corrosion is a complex phenomenon, and it is not possible to give specific rules for the estimation of the corrosion allowance required for all circumstances. The allowance should be based on experience with the material of construction under similar service conditions to those for the proposed design. For carbon and low-alloy steels, where severe corrosion is not expected, a minimum allowance of 2.0 mm should be used; where more severe conditions are anticipated this should be increased to 4.0 mm. Most design codes and standards specify a minimum allowance of 1.0 mm.

### 13.4.7. Design loads

A structure must be designed to resist gross plastic deformation and collapse under all the conditions of loading. The loads to which a process vessel will be subject in service are listed below. They can be classified as major loads, that must always be considered in vessel design, and subsidiary loads. Formal stress analysis to determine the effect of the subsidiary loads is only required in the codes and standards where it is not possible to demonstrate the adequacy of the proposed design by other means; such as by comparison with the known behaviour of existing vessels.

#### **Major loads**

1. Design pressure: including any significant static head of liquid.
2. Maximum weight of the vessel and contents, under operating conditions.
3. Maximum weight of the vessel and contents under the hydraulic test conditions.
4. Wind loads.
5. Earthquake (seismic) loads.
6. Loads supported by, or reacting on, the vessel.

#### **Subsidiary loads**

1. Local stresses caused by supports, internal structures and connecting pipes.
2. Shock loads caused by water hammer, or by surging of the vessel contents.
3. Bending moments caused by eccentricity of the centre of the working pressure relative to the neutral axis of the vessel.
4. Stresses due to temperature differences and differences in the coefficient expansion of materials.
5. Loads caused by fluctuations in temperature and pressure.

A vessel will not be subject to all these loads simultaneously. The designer must determine what combination of possible loads gives the worst situation, and design for that loading condition.

### 13.4.8. Minimum practical wall thickness

There will be a minimum wall thickness required to ensure that any vessel is sufficiently rigid to withstand its own weight, and any incidental loads. As a general guide the wall thickness of any vessel should not be less than the values given below; the values include a corrosion allowance of 2 mm:

Vessel diameter (m)	Minimum thickness (mm)
1	5
1 to 2	7
2 to 2.5	9
2.5 to 3.0	10
3.0 to 3.5	12

## 13.5. THE DESIGN OF THIN-WALLED VESSELS UNDER INTERNAL PRESSURE

### 13.5.1. Cylinders and spherical shells

For a cylindrical shell the minimum thickness required to resist internal pressure can be determined from equation 13.7; the cylindrical stress will be the greater of the two principal stresses.

If  $D_i$  is internal diameter and  $e$  the minimum thickness required, the mean diameter will be  $(D_i + e)$ ; substituting this for  $D$  in equation 13.7 gives:

$$e = \frac{P_i(D_i + e)}{2f}$$

where  $f$  is the design stress and  $P_i$  the internal pressure. Rearranging gives:

$$e = \frac{P_i D_i}{2f - P_i} \quad (13.39)$$

This is the form of the equation given in the British Standard PD 5500.

An equation for the minimum thickness of a sphere can be obtained from equation 13.9:

$$e = \frac{P_i D_i}{4f - P_i} \quad (13.40)$$

The equation for a sphere given in BS 5500 is:

$$e = \frac{P_i D_i}{4f - 1.2P_i} \quad (13.41)$$

The equation given in the British Standard PD 5500 differs slightly from equation 13.40, as it is derived from the formula for thick-walled vessels; see Section 13.15.

If a welded joint factor is used equations 13.39 and 13.40 are written:

$$e = \frac{P_i D_i}{2Jf - P_i} \quad (13.39a)$$

and

$$e = \frac{P_i D_i}{4Jf - 1.2P_i} \quad (13.40b)$$

where  $J$  is the joint factor.

Any consistent set of units can be used for equations 13.39a to 13.40b.

### 13.5.2. Heads and closures

The ends of a cylindrical vessel are closed by heads of various shapes. The principal types used are:

1. Flat plates and formed flat heads; Figure 13.9.
2. Hemispherical heads; Figure 13.10a.
3. Ellipsoidal heads; Figure 13.10b.
4. Torispherical heads; Figure 13.10c.



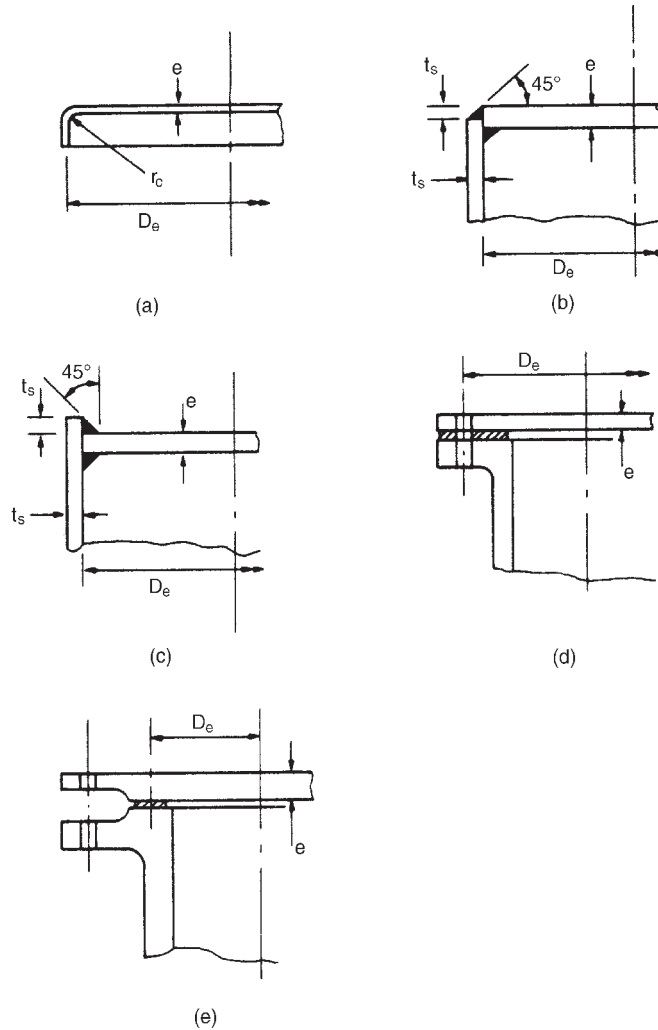


Figure 13.9. Flat-end closures (a) Flanged plate (b) Welded plate (c) Welded plate (d) Bolted cover (e) Bolted cover

Hemispherical, ellipsoidal and torispherical heads are collectively referred to as domed heads. They are formed by pressing or spinning; large diameters are fabricated from formed sections. Torispherical heads are often referred to as dished ends.

The preferred proportions of domed heads are given in the standards and codes.

### **Choice of closure**

Flat plates are used as covers for manways, and as the channel covers of heat exchangers. Formed flat ends, known as “flange-only” ends, are manufactured by turning over a flange with a small radius on a flat plate, Figure 13.9a. The corner radius reduces the abrupt

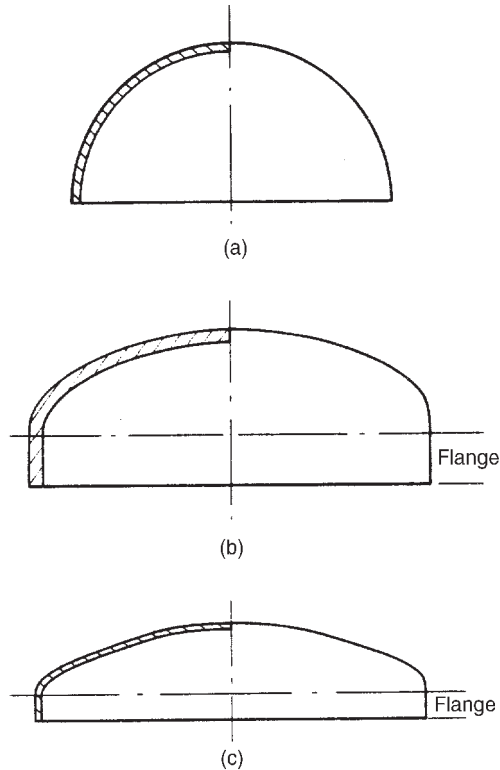


Figure 13.10. Domed heads (a) Hemispherical (b) Ellipsoidal (c) Torispherical

change of shape, at the junction with the cylindrical section; which reduces the local stresses to some extent: “Flange-only” heads are the cheapest type of formed head to manufacture, but their use is limited to low-pressure and small-diameter vessels.

Standard torispherical heads (dished ends) are the most commonly used end closure for vessels up to operating pressures of 15 bar. They can be used for higher pressures, but above 10 bar their cost should be compared with that of an equivalent ellipsoidal head. Above 15 bar an ellipsoidal head will usually prove to be the most economical closure to use.

A hemispherical head is the strongest shape; capable of resisting about twice the pressure of a torispherical head of the same thickness. The cost of forming a hemispherical head will, however, be higher than that for a shallow torispherical head. Hemispherical heads are used for high pressures.

### 13.5.3. Design of flat ends

Though the fabrication cost is low, flat ends are not a structurally efficient form, and very thick plates would be required for high pressures or large diameters.

The design equations used to determine the thickness of flat ends are based on the analysis of stresses in flat plates; Section 13.3.5.

The thickness required will depend on the degree of constraint at the plate periphery. The minimum thickness required is given by:

$$e = C_p D_e \sqrt{\frac{P_i}{f}} \quad (13.42)$$

where  $C_p$  = a design constant, dependent on the edge constraint,  
 $D_e$  = nominal plate diameter,  
 $f$  = design stress.

Any consistent set of units can be used.

Values for the design constant  $C_p$  and the nominal plate diameter  $D_e$  are given in the design codes and standards for various arrangements of flat end closures.

The values of the design constant and nominal diameter for the typical designs shown in Figure 13.9 are given below:

- (a) Flanged-only end, for diameters less than 0.6 m and corner radii at least equal to  $0.25e$ ,  $C_p$  can be taken as 0.45;  $D_e$  is equal to  $D_i$ .
- (b, c) Plates welded to the end of the shell with a fillet weld, angle of fillet  $45^\circ$  and depth equal to the plate thickness, take  $C_p$  as 0.55 and  $D_e = D_i$ .
- (d) Bolted cover with a full face gasket (see Section 13.10), take  $C_p = 0.4$  and  $D_e$  equal to the bolt circle diameter.
- (e) Bolted end cover with a narrow-face gasket, take  $C_p = 0.55$  and  $D_e$  equal to the mean diameter of the gasket.

#### 13.5.4. Design of domed ends

Design equations and charts for the various types of domed heads are given in the codes and standards and should be used for detailed design. The codes and standards cover both unpierced and pierced heads. Pierced heads are those with openings or connections. The head thickness must be increased to compensate for the weakening effect of the holes where the opening or branch is not locally reinforced (see Section 13.6).

For convenience, simplified design equations are given in this section. These are suitable for the preliminary sizing of unpierced heads and for heads with fully compensated openings or branches.

#### ***Hemispherical heads***

It can be seen by examination of equations 13.7 and 13.9, that for equal stress in the cylindrical section and hemispherical head of a vessel the thickness of the head need only be half that of the cylinder. However, as the dilation of the two parts would then be different, discontinuity stresses would be set up at the head and cylinder junction. For no difference in dilation between the two parts (equal diametrical strain) it can be shown that for steels (Poisson's ratio = 0.3) the ratio of the hemispherical head thickness to cylinder

thickness should be  $7/17$ . However, the stress in the head would then be greater than that in the cylindrical section; and the optimum thickness ratio is normally taken as 0.6; see Brownell and Young (1959).

### ***Ellipsoidal heads***

Most standard ellipsoidal heads are manufactured with a major and minor axis ratio of 2 : 1. For this ratio, the following equation can be used to calculate the minimum thickness required:

$$e = \frac{P_i D_i}{2Jf - 0.2P_i} \quad (13.43)$$

### ***Torispherical heads***

There are two junctions in a torispherical end closure: that between the cylindrical section and the head, and that at the junction of the crown and the knuckle radii. The bending and shear stresses caused by the differential dilation that will occur at these points must be taken into account in the design of the heads. One approach taken is to use the basic equation for a hemisphere and to introduce a stress concentration, or shape, factor to allow for the increased stress due to the discontinuity. The stress concentration factor is a function of the knuckle and crown radii.

$$e = \frac{P_i R_c C_s}{2fJ + P_i(C_s - 0.2)} \quad (13.44)$$

where  $C_s$  = stress concentration factor for torispherical heads =  $\frac{1}{4}(3 + \sqrt{R_c/R_k})$ ,  
 $R_c$  = crown radius,  
 $R_k$  = knuckle radius.

The ratio of the knuckle to crown radii should not be less than 0.06, to avoid buckling; and the crown radius should not be greater than the diameter of the cylindrical section. Any consistent set of units can be used with equations 13.43 and 13.44. For formed heads (no joints in the head) the joint factor  $J$  is taken as 1.0.

### ***Flanges (skirts) on domed heads***

Formed domed heads are made with a short straight cylindrical section, called a flange or skirt; Figure 13.10. This ensures that the weld line is away from the point of discontinuity between the head and the cylindrical section of the vessel.

## **13.5.5. Conical sections and end closures**

Conical sections (reducers) are used to make a gradual reduction in diameter from one cylindrical section to another of smaller diameter.

Conical ends are used to facilitate the smooth flow and removal of solids from process equipment; such as, hoppers, spray-dryers and crystallisers.

From equation 13.10 it can be seen that the thickness required at any point on a cone is related to the diameter by the following expression:

$$e = \frac{P_i D_c}{2fJ - P_i} \cdot \frac{1}{\cos \alpha} \quad (13.45)$$

where  $D_c$  is the diameter of the cone at the point,  
 $\alpha$  = half the cone apex angle.

This equation will only apply at points away from the cone to cylinder junction. Bending and shear stresses will be caused by the different dilation of the conical and cylindrical sections. This can be allowed for by introducing a stress concentration factor, in a similar manner to the method used for torispherical heads,

$$e = \frac{C_c P_i D_c}{2fJ - P_i} \quad (13.46)$$

The design factor  $C_c$  is a function of the half apex angle  $\alpha$ :

$\alpha$	20°	30°	45°	60°
$C_c$	1.00	1.35	2.05	3.20

A formed section would normally be used for the transition between a cylindrical section and conical section; except for vessels operating at low pressures, or under hydrostatic pressure only. The transition section would be made thicker than the conical or cylindrical section and formed with a knuckle radius to reduce the stress concentration at the transition, Figure 13.11. The thickness at the knuckle can be calculated using equation 13.46, and that for the conical section away from the transition from equation 13.45.

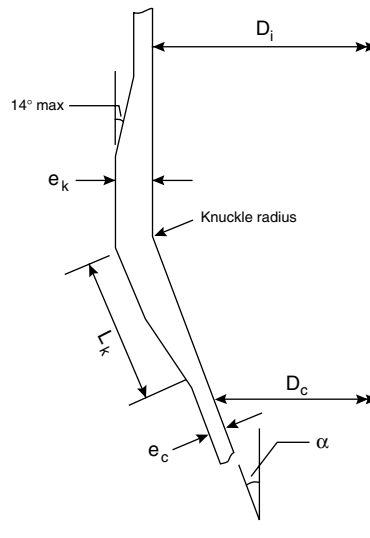


Figure 13.11. Conical transition section

The length of the thicker section  $L_k$  depends on the cone angle and is given by:

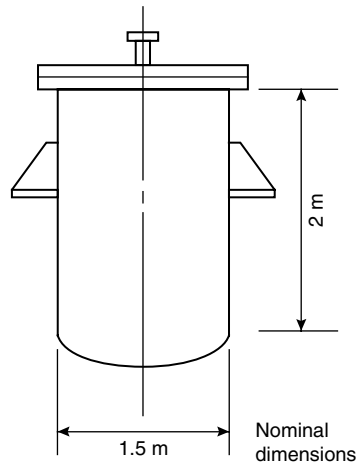
$$L_k = \sqrt{\frac{D_i e_k}{4 \cos \alpha}} \quad (13.47)$$

where  $e_k$  is the thickness at the knuckle.

Design procedures for conical sections are given in the codes and standards.

### Example 13.1

Estimate the thickness required for the component parts of the vessel shown in the diagram. The vessel is to operate at a pressure of 14 bar (absolute) and temperature of 300°C. The material of construction will be plain carbon steel. Welds will be fully radiographed. A corrosion allowance of 2 mm should be used.



### Solution

Design pressure, take as 10 per cent above operating pressure,

$$= (14 - 1) \times 1.1$$

$$= 14.3 \text{ bar}$$

$$= 1.43 \text{ N/mm}^2$$

Design temperature 300°C.

From Table 13.2, typical design stress = 85 N/mm<sup>2</sup>.

### Cylindrical section

$$e = \frac{1.43 \times 1.5 \times 10^3}{2 \times 85 - 1.43} = 12.7 \text{ mm} \quad (13.39)$$

add corrosion allowance  $12.7 + 2 = 14.7$

say 15 mm plate

**Domed head**

(i) Try a standard dished head (torisphere):

$$\text{crown radius } R_c = D_i = 1.5 \text{ m}$$

$$\text{knuckle radius} = 6 \text{ per cent } R_c = 0.09 \text{ m}$$

A head of this size would be formed by pressing: no joints, so  $J = 1$ .

$$C_s = \frac{1}{4} \left( 3 + \sqrt{\frac{R_c}{R_k}} \right) = \frac{1}{4} \left( 3 + \sqrt{\frac{1.5}{0.09}} \right) = 1.77 \quad (13.44)$$

$$e = \frac{1.43 \times 1.5 \times 10^3 \times 1.77}{2 \times 85 + 1.43(1.77 - 0.2)} = \underline{\underline{22.0 \text{ mm}}} \quad (13.44)$$

(ii) Try a “standard” ellipsoidal head, ratio major : minor axes = 2 : 1

$$\begin{aligned} e &= \frac{1.43 \times 1.5 \times 10^3}{2 \times 85 - 0.2 \times 1.43} \\ &= \underline{\underline{12.7 \text{ mm}}} \end{aligned} \quad (13.43)$$

So an ellipsoidal head would probably be the most economical. Take as same thickness as wall 15 mm.

**Flat head**

Use a full face gasket  $C_p = 0.4$

$D_e$  = bolt circle diameter, take as approx. 1.7 m.

$$e = 0.4 \times 1.7 \times 10^3 \sqrt{\frac{1.43}{85}} = \underline{\underline{88.4 \text{ mm}}} \quad (13.42)$$

Add corrosion allowance and round-off to 90 mm.

This shows the inefficiency of a flat cover. It would be better to use a flanged domed head.

**13.6. COMPENSATION FOR OPENINGS AND BRANCHES**

All process vessels will have openings for connections, manways, and instrument fittings. The presence of an opening weakens the shell, and gives rise to stress concentrations. The stress at the edge of a hole will be considerably higher than the average stress in the surrounding plate. To compensate for the effect of an opening, the wall thickness is increased in the region adjacent to the opening. Sufficient reinforcement must be provided to compensate for the weakening effect of the opening without significantly altering the general dilation pattern of the vessel at the opening. Over-reinforcement will reduce the flexibility of the wall, causing a “hard spot”, and giving rise to secondary stresses; typical arrangements are shown in Figure 13.12.

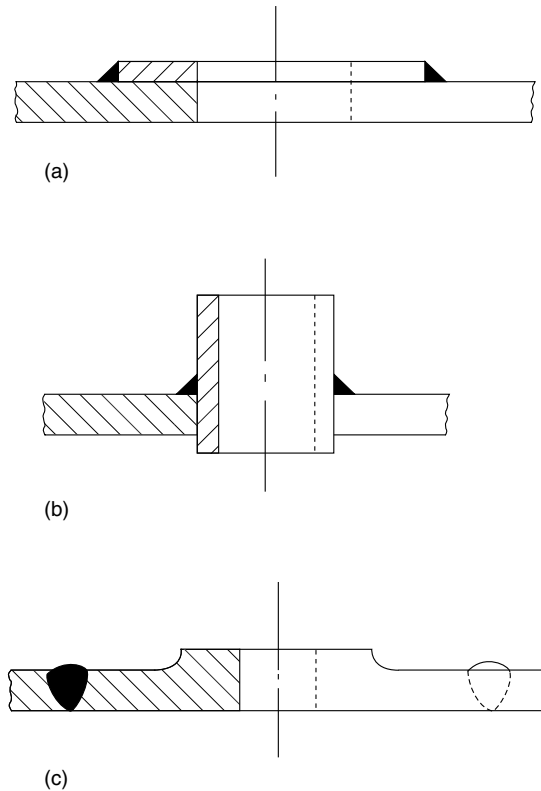


Figure 13.12. Types of compensation for openings (a) Welded pad (b) Inset nozzle (c) Forged ring

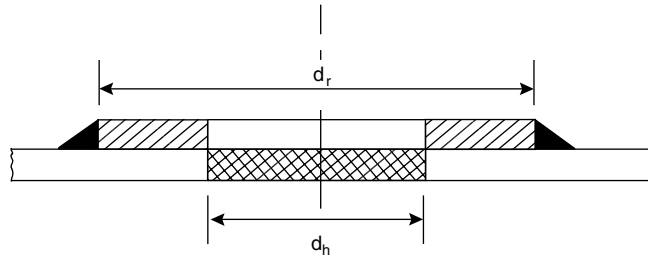
The simplest method of providing compensation is to weld a pad or collar around the opening, Figure 13.12a. The outer diameter of the pad is usually between  $1\frac{1}{2}$  to 2 times the diameter of the hole or branch. This method, however, does not give the best disposition of the reinforcing material about the opening, and in some circumstances high thermal stress can arise due to the poor thermal conductivity of the pad to shell junction.

At a branch, the reinforcement required can be provided, with or without a pad, by allowing the branch, to protrude into the vessel, Figure 13.12b. This arrangement should be used with caution for process vessels, as the protrusion will act as a trap for crud, and local corrosion can occur. Forged reinforcing rings, Figure 13.12c, provide the most effective method of compensation, but are expensive. They would be used for any large openings and branches in vessels operating under severe conditions.

### **Calculation of reinforcement required**

The “equal area method” is the simplest method used for calculating the amount of reinforcement required, and is allowed in most design codes and standards. The principle used is to provide reinforcement local to the opening, equal in cross-sectional area to the area removed in forming the opening, Figure 13.13. If the actual thickness of the vessel







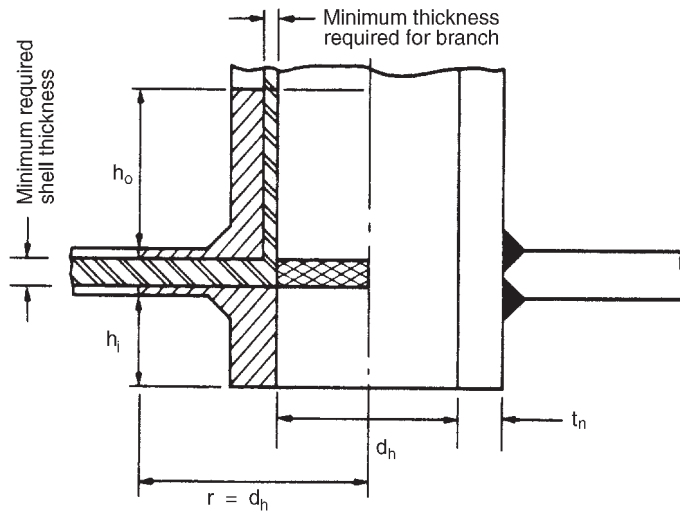


-   $A_1 = \text{Area removed}$
-   $A_2 = \text{reinforcement area}$
- $A_2 = A_1$
- $d_r = 1.5 \text{ to } 2.0 \times d_h$

Figure 13.13. Equal-area method of compensation



-   $A_1$  Area removed
-   $A_2$  Area allowed as compensation
- $A_2 = A_1$

$$\text{Max. allowed } h_0 \text{ and } h_i = 0.64 \sqrt{(d_h + t_n)t_n}$$

All dimensions shown are in the fully corroded condition (i.e. less corrosion allowance)

Figure 13.14. Branch compensation

wall is greater than the minimum required to resist the loading, the excess thickness can be taken into account when estimating the area of reinforcement required. Similarly with a branch connection, if the wall thickness of the branch or nozzle is greater than the minimum required, the excess material in the branch can be taken into account. Any corrosion allowance must be deducted when determining the excess thickness available as compensation. The standards and codes differ in the areas of the branch and shell considered to be effective for reinforcement, and should be consulted to determine the actual area allowed and the disposition of the various types of reinforcement. Figure 13.14 can be used for preliminary calculations. For branch connections of small diameter the reinforcement area can usually be provided by increasing the wall thickness of the branch pipe. Some design codes and standards do not require compensation for connections below 89 mm (3 in.) diameter.

If anything, the equal area method tends to over-estimate the compensation required and in some instances the additional material can reduce the fatigue life of the vessel. More sophisticated methods for determining the compensation required have been introduced into the latest editions of the codes and standards.

The equal-area method is generally used for estimating the increase in thickness required to compensate for multiple openings.

## 13.7. DESIGN OF VESSELS SUBJECT TO EXTERNAL PRESSURE

### 13.7.1. Cylindrical shells

Two types of process vessel are likely to be subjected to external pressure: those operated under vacuum, where the maximum pressure will be 1 bar (atm); and jacketed vessels, where the inner vessel will be under the jacket pressure. For jacketed vessels, the maximum pressure difference should be taken as the full jacket pressure, as a situation may arise in which the pressure in the inner vessel is lost. Thin-walled vessels subject to external pressure are liable to failure through elastic instability (buckling) and it is this mode of failure that determines the wall thickness required.

For an open-ended cylinder, the critical pressure to cause buckling  $P_c$  is given by the following expression; see Windenburg and Trilling (1934):

$$P_c = \frac{1}{3} \left[ n^2 - 1 + \frac{2n^2 - 1 - \nu}{n^2 \left( \frac{2L}{\pi D_0} \right)^2 - 1} \right] \frac{2E}{(1 - \nu^2)} \left( \frac{t}{D_0} \right)^3 + \frac{2Et/D_0}{(n^2 - 1) \left[ n^2 \left( \frac{2L}{\pi D_0} \right)^2 + 1 \right]^2} \quad (13.48)$$

where  $L$  = the unsupported length of the vessel, the effective length,

$D_0$  = external diameter,

$t$  = wall thickness,

$E$  = Young's modulus,

$\nu$  = Poisson's ratio,

$n$  = the number of lobes formed at buckling.

For long tubes and cylindrical vessels this expression can be simplified by neglecting terms with the group  $(2L/\pi D_0)^2$  in the denominator; the equation then becomes:

$$P_c = \frac{1}{3} \left[ (n^2 - 1) \frac{2E}{(1 - \nu^2)} \right] \left( \frac{t}{D_0} \right)^3 \quad (13.49)$$

The minimum value of the critical pressure will occur when the number of lobes is 2, and substituting this value into equation 13.49 gives:

$$P_c = \frac{2E}{1 - \nu^2} \left( \frac{t}{D_0} \right)^3 \quad (13.50)$$

For most pressure-vessel materials Poisson's ratio can be taken as 0.3; substituting this in equation 13.50 gives:

$$P_c = 2.2E \left( \frac{t}{D_0} \right)^3 \quad (13.51)$$

For short closed vessels, and long vessels with stiffening rings, the critical buckling pressure will be higher than that predicted by equation 13.51. The effect of stiffening can be taken into account by introducing a "collapse coefficient",  $K_c$ , into equation 13.51.

$$P_c = K_c E \left( \frac{t}{D_0} \right)^3 \quad (13.52)$$

where  $K_c$  is a function of the diameter and thickness of the vessel, and the effective length  $L'$  between the ends or stiffening rings; and is obtained from Figure 13.16. The effective length for some typical arrangements is shown in Figure 13.15.

It can be shown (see Southwell, 1913) that the critical distance between stiffeners,  $L_c$ , beyond which stiffening will not be effective is given by:

$$L_c = \frac{4\pi\sqrt{6}D_0}{27} \left[ (1 - \nu^2)^{1/4} \right] \left( \frac{D_0}{t} \right)^{1/2} \quad (13.53)$$

Substituting  $\nu = 0.3$  gives:

$$L_c = 1.11D_0 \left( \frac{D_0}{t} \right)^{1/2} \quad (13.54)$$

Any stiffening rings used must be spaced closer than  $L_c$ . Equation 13.52 can be used to determine the critical buckling pressure and hence the thickness required to resist a given external pressure; see Example 13.2. A factor of safety of at least 3 should be applied to the values predicted using equation 13.52.

The design methods and design curves given in the standards and codes should be used for the detailed design of vessels subject to external pressure.

### **Out of roundness**

Any out-of-roundness in a shell after fabrication will significantly reduce the ability of the vessel to resist external pressure. A deviation from a true circular cross-section equal

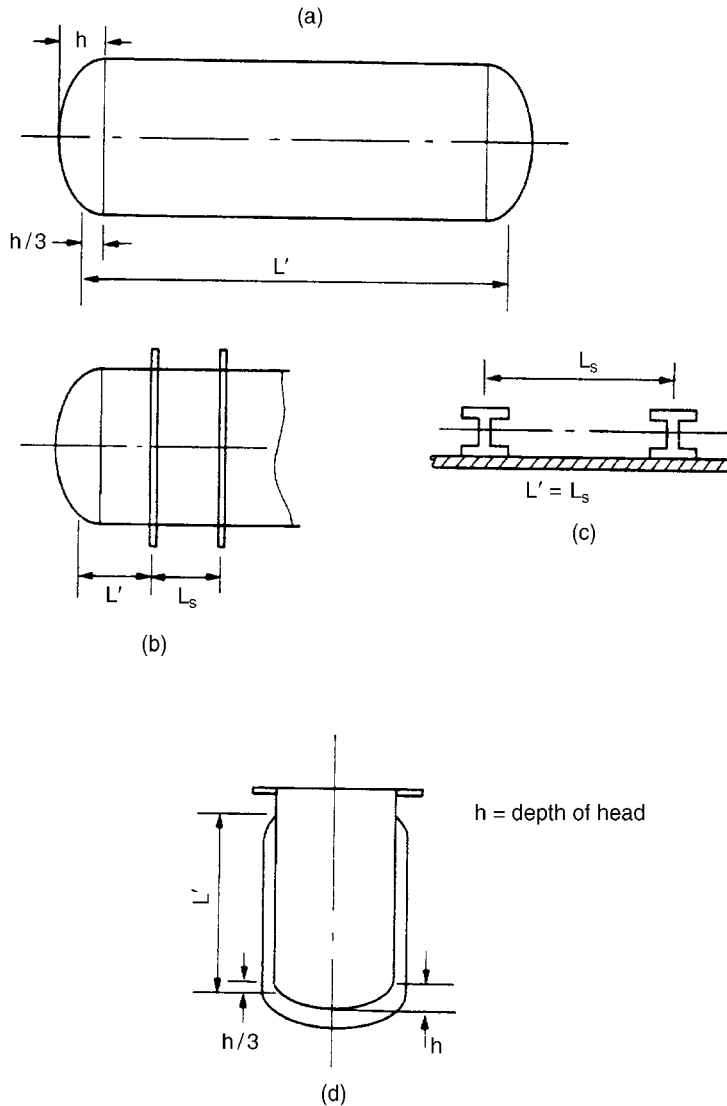


Figure 13.15. Effective length, vessel under external pressure (a) Plain vessel (b) With stiffeners (use smaller of  $L'$  and  $L_s$ ) (c) I-section stiffening rings (d) Jacketed vessel

to the shell thickness will reduce the critical buckling pressure by about 50 per cent. The ovality (out-of-roundness) of a cylinder is measured by:

$$\text{Ovality} = \frac{2(D_{\max} - D_{\min})}{(D_{\max} + D_{\min})} \times 100, \text{ per cent}$$

For vessels under external pressure this should not normally exceed 1.5 per cent.

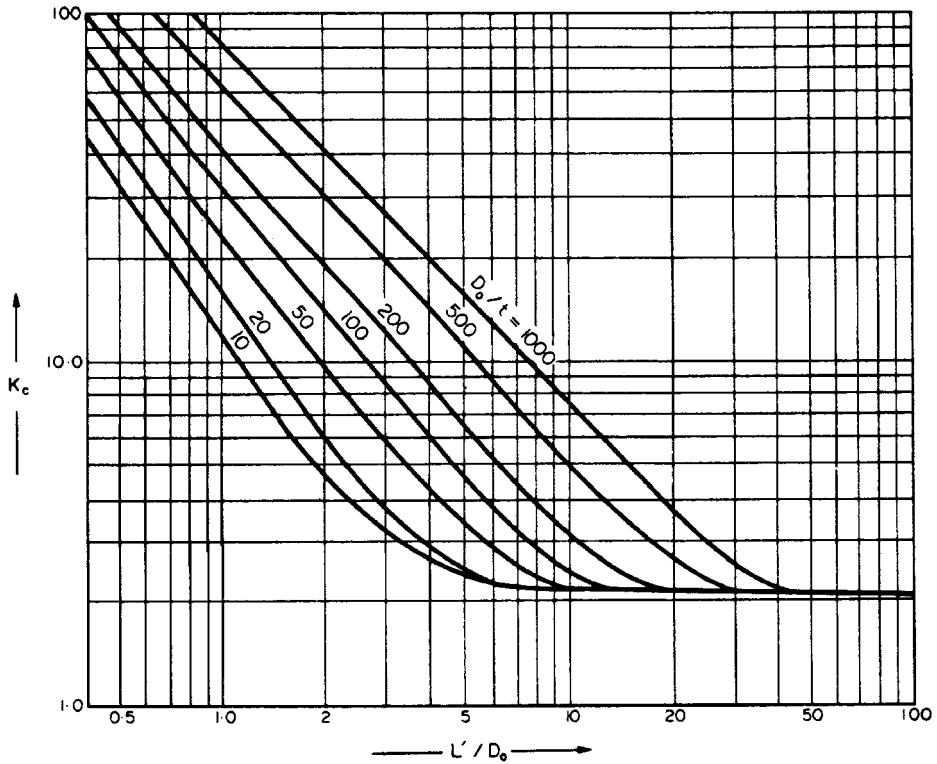


Figure 13.16. Collapse coefficients for cylindrical shells (after Brownell and Young, 1959)

### 13.7.2. Design of stiffness rings

The usual procedure is to design stiffening rings to carry the pressure load for a distance of  $\frac{1}{2}L_s$  on each side of the ring, where  $L_s$  is the spacing between the rings. So, the load per unit length on a ring  $F_r$  will be given by:

$$F_r = P_e L_s \quad (13.55)$$

where  $P_e$  is the external pressure.

The critical load to cause buckling in a ring under a uniform radial load  $F_c$  is given by the following expression

$$F_c = \frac{24EI_r}{D_r^3} \quad (13.56)$$

where  $I_r$  = second moment of area of the ring cross-section,

$D_r$  = diameter of the ring (approximately equal to the shell outside diameter).

Combining equations 13.55 and 13.56 will give an equation from which the required dimensions of the ring can be determined:

$$P_e L_s \not\prec \frac{24EI_r}{D_r^3} \div (\text{factor of safety}) \quad (13.57)$$

In calculating the second moment of area of the ring some allowance is normally made for the vessel wall; the use of  $I_r$  calculated for the ring alone will give an added factor of safety.

In vacuum distillation columns, the plate-support rings will act as stiffening rings and strengthen the vessel; see Example 13.2.

### 13.7.3. Vessel heads

The critical buckling pressure for a sphere subject to external pressure is given by (see Timoshenko, 1936):

$$P_c = \frac{2Et^2}{R_s^2 \sqrt{3(1-\nu^2)}} \quad (13.58)$$

where  $R_s$  is the outside radius of the sphere. Taking Poisson's ratio as 0.3 gives:

$$P_c = 1.21E \left( \frac{t}{R_s} \right)^2 \quad (13.59)$$

This equation gives the critical pressure required to cause general buckling; local buckling can occur at a lower pressure. Karman and Tsien (1939) have shown that the pressure to cause a "dimple" to form is about one-quarter of that given by equation 13.59, and is given by:

$$P'_c = 0.365E \left( \frac{t}{R_s} \right)^2 \quad (13.60)$$

A generous factor of safety is needed when applying equation 13.60 to the design of heads under external pressure. A value of 6 is typically used, which gives the following equation for the minimum thickness:

$$e = 4R_s \sqrt{\left( \frac{P_e}{E} \right)} \quad (13.61)$$

Any consistent system of units can be used with equation 13.61.

Torispherical and ellipsoidal heads can be designed as equivalent hemispheres. For a torispherical head the radius  $R_s$  is taken as equivalent to the crown radius  $R_c$ . For an ellipsoidal head the radius can be taken as the maximum radius of curvature; that at the top, given by:

$$R_s = \frac{a^2}{b} \quad (13.62)$$

where  $2a$  = major axis =  $D_0$  (shell o.d.),

$2b$  = minor axis =  $2h$ ,

$h$  = height of the head from the tangent line.

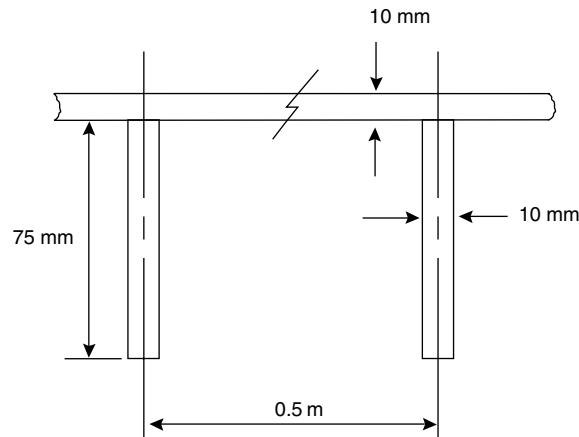
Because the radius of curvature of an ellipse is not constant the use of the maximum radius will over-size the thickness required.

Design methods for heads under external pressure are given in the standards and codes.

### Example 13.2

A vacuum distillation column is to operate under a top pressure of 50 mmHg. The plates are supported on rings 75 mm wide, 10 mm deep. The column diameter is 1 m and the plate spacing 0.5 m. Check if the support rings will act as effective stiffening rings. The material of construction is carbon steel and the maximum operating temperature 50°C. If the vessel thickness is 10 mm, check if this is sufficient.

### Solution



Take the design pressure as 1 bar external.

From equation 13.55 the load on each ring =  $0.5 \times 10^5$  N/m.

Taking  $E$  for steel at 50°C as  $200,000 \text{ N/mm}^2 = 2 \times 10^{11} \text{ N/m}^2$ , and using a factor of safety of 6, the second moment of area of the ring to avoid buckling is given by: equation 13.57

$$0.5 \times 10^5 = \frac{24 \times 2 \times 10^{11} \times I_r}{1^3 \times 6}$$

$$I_r = 6.25 \times 10^{-8} \text{ m}^4$$

For a rectangular section, the second moment of area is given by

$$I = \frac{\text{breadth} \times \text{depth}^3}{12}$$

$$\text{so } I_r \text{ for the support rings} = \frac{10 \times (75)^3 \times 10^{-12}}{12}$$

$$= 3.5 \times 10^{-7} \text{ m}^4$$

and the support ring is of an adequate size to be considered as a stiffening ring.

$$\frac{L'}{D_0} = \frac{0.5}{1} = 0.5$$

$$\frac{D_0}{t} = \frac{1000}{10} = 100$$

From Figure 13.16  $K_c = 75$

From equation 13.52

$$P_c = 75 \times 2 \times 10^{11} \left( \frac{1}{100} \right)^3 = \underline{\underline{15 \times 10^6 \text{ N/m}^2}}$$

which is well above the maximum design pressure of  $10^5 \text{ N/m}^2$ .

### 13.8. DESIGN OF VESSELS SUBJECT TO COMBINED LOADING

Pressure vessels are subjected to other loads in addition to pressure (see Section 13.4.7) and must be designed to withstand the worst combination of loading without failure. It is not practical to give an explicit relationship for the vessel thickness to resist combined loads. A trial thickness must be assumed (based on that calculated for pressure alone) and the resultant stress from all loads determined to ensure that the maximum allowable stress intensity is not exceeded at any point.

The main sources of load to consider are:

1. Pressure.
2. Dead weight of vessel and contents.
3. Wind.
4. Earthquake (seismic).
5. External loads imposed by piping and attached equipment.

The primary stresses arising from these loads are considered in the following paragraphs, for cylindrical vessels; Figure 13.17.

#### **Primary stresses**

1. The longitudinal and circumferential stresses due to pressure (internal or external), given by:

$$\sigma_h = \frac{PD_i}{2t} \quad (13.63)$$

$$\sigma_L = \frac{PD_i}{4t} \quad (13.64)$$

2. The direct stress  $\sigma_w$  due to the weight of the vessel, its contents, and any attachments. The stress will be tensile (positive) for points below the plane of the vessel supports, and compressive (negative) for points above the supports, see Figure 13.18. The dead-weight stress will normally only be significant, compared to the magnitude of the other stresses, in tall vessels.



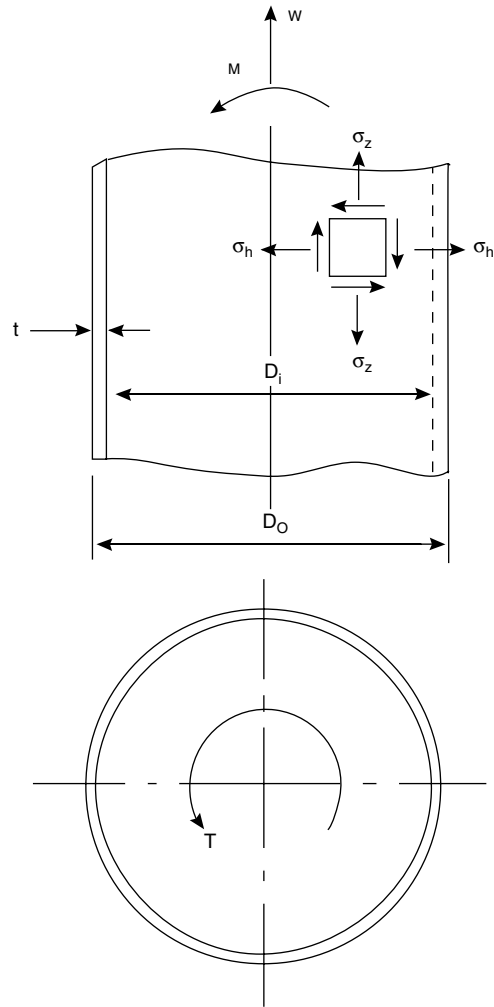


Figure 13.17. Stresses in a cylindrical shell under combined loading

$$\sigma_w = \frac{W}{\pi(D_i + t)t} \quad (13.65)$$

where  $W$  is the total weight which is supported by the vessel wall at the plane considered, see Section 13.8.1.

3. Bending stresses resulting from the bending moments to which the vessel is subjected. Bending moments will be caused by the following loading conditions:
  - (a) The wind loads on tall self-supported vessels (Section 13.8.2).
  - (b) Seismic (earthquake) loads on tall vessels (Section 13.8.3).
  - (c) The dead weight and wind loads on piping and equipment which is attached to the vessel, but offset from the vessel centre line (Section 13.8.4).

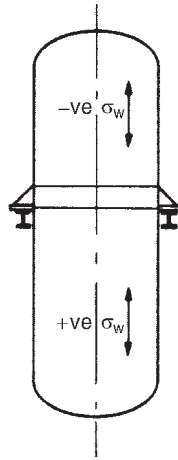


Figure 13.18. Stresses due to dead-weight loads

(d) For horizontal vessels with saddle supports, from the disposition of dead-weight load (see Section 13.9.1).

The bending stresses will be compressive or tensile, depending on location, and are given by:

$$\sigma_b = \pm \frac{M}{I_v} \left( \frac{D_i}{2} + t \right) \quad (13.66)$$

where  $M_v$  is the total bending moment at the plane being considered and  $I_v$  the second moment of area of the vessel about the plane of bending.

$$I_v = \frac{\pi}{64} (D_0^4 - D_i^4) \quad (13.67)$$

4. Torsional shear stresses  $\tau$  resulting from torque caused by loads offset from the vessel axis. These loads will normally be small, and need not be considered in preliminary vessel designs.

The torsional shear stress is given by:

$$\tau = \frac{T}{I_p} \left( \frac{D_i}{2} + t \right) \quad (13.68)$$

where  $T$  = the applied torque,

$$I_p = \text{polar second moment of area} = (\pi/32)(D_0^4 - D_i^4)$$

### **Principal stresses**

The principal stresses will be given by:

$$\sigma_1 = \frac{1}{2} [\sigma_h + \sigma_z + \sqrt{(\sigma_h - \sigma_z)^2 + 4\tau^2}] \quad (13.69)$$

$$\sigma_2 = \frac{1}{2}[\sigma_h + \sigma_z - \sqrt{(\sigma_h - \sigma_z)^2 + 4\tau^2}] \quad (13.70)$$

where  $\sigma_z$  = total longitudinal stress

$$= \sigma_L + \sigma_w \pm \sigma_b$$

$\sigma_w$  should be counted as positive if tension and negative if compressive.

$\tau$  is not usually significant.

The third principal stress, that in the radial direction  $\sigma_3$ , will usually be negligible for thin-walled vessels (see Section 13.1.1). As an approximation it can be taken as equal to one-half the pressure loading

$$\sigma_3 = 0.5P \quad (13.71)$$

$\sigma_3$  will be compressive (negative).

### ***Allowable stress intensity***

The maximum intensity of stress allowed will depend on the particular theory of failure adopted in the design method (see Section 13.3.2). The maximum shear-stress theory is normally used for pressure vessel design.

Using this criterion the maximum stress intensity at any point is taken for design purposes as the numerically greatest value of the following:

$$(\sigma_1 - \sigma_2)$$

$$(\sigma_1 - \sigma_3)$$

$$(\sigma_2 - \sigma_3)$$

The vessel wall thickness must be sufficient to ensure the maximum stress intensity does not exceed the design stress (nominal design strength) for the material of construction, at any point.

### ***Compressive stresses and elastic stability***

Under conditions where the resultant axial stress  $\sigma_z$  due to the combined loading is compressive, the vessel may fail by elastic instability (buckling) (see Section 13.3.3). Failure can occur in a thin-walled process column under an axial compressive load by buckling of the complete vessel, as with a strut (Euler buckling); or by local buckling, or wrinkling, of the shell plates. Local buckling will normally occur at a stress lower than that required to buckle the complete vessel. A column design must be checked to ensure that the maximum value of the resultant axial stress does not exceed the critical value at which buckling will occur.

For a curved plate subjected to an axial compressive load the critical buckling stress  $\sigma_c$  is given by (see Timoshenko, 1936):

$$\sigma_c = \frac{E}{\sqrt{3(1 - \nu^2)}} \left( \frac{t}{R_p} \right) \quad (13.72)$$

where  $R_p$  is the radius of curvature.

Taking Poisson's ratio as 0.3 gives:

$$\sigma_c = 0.60E \left( \frac{t}{R_p} \right) \quad (13.73)$$

By applying a suitable factor of safety, equation 13.72 can be used to predict the maximum allowable compressive stress to avoid failure by buckling. A large factor of safety is required, as experimental work has shown that cylindrical vessels will buckle at values well below that given by equation 13.72. For steels at ambient temperature  $E = 200,000 \text{ N/mm}^2$ , and equation 13.72 with a factor of safety of 12 gives:

$$\sigma_c = 2 \times 10^4 \left( \frac{t}{D_o} \right) \text{ N/mm}^2 \quad (13.74)$$

The maximum compressive stress in a vessel wall should not exceed that given by equation 13.74; or the maximum allowable design stress for the material, whichever is the least.

### **Stiffening**

As with vessels under external pressure, the resistance to failure buckling can be increased significantly by the use of stiffening rings, or longitudinal strips. Methods for estimating the critical buckling stress for stiffened vessels are given in the standards and codes.

### **Loading**

The loads to which a vessel may be subjected will not all occur at the same time. For example, it is the usual practice to assume that the maximum wind load will not occur simultaneously with a major earthquake.

The vessel must be designed to withstand the worst combination of the loads likely to occur in the following situations:

1. During erection (or dismantling) of the vessel.
2. With the vessel erected but not operating.
3. During testing (the hydraulic pressure test).
4. During normal operation.

#### **13.8.1. Weight loads**

The major sources of dead weight loads are:

1. The vessel shell.
2. The vessel fittings: manways, nozzles.
3. Internal fittings: plates (plus the fluid on the plates); heating and cooling coils.
4. External fittings: ladders, platforms, piping.
5. Auxiliary equipment which is not self-supported; condensers, agitators.
6. Insulation.

7. The weight of liquid to fill the vessel. The vessel will be filled with water for the hydraulic pressure test; and may fill with process liquid due to misoperation.

*Note:* for vessels on a skirt support (see Section 13.9.2), the weight of the liquid to fill the vessel will be transferred directly to the skirt.

The weight of the vessel and fittings can be calculated from the preliminary design sketches. The weights of standard vessel components: heads, shell plates, manways, branches and nozzles, are given in various handbooks; Megyesy (2001) and Brownell and Young (1959).

For preliminary calculations the approximate weight of a cylindrical vessel with domed ends, and uniform wall thickness, can be estimated from the following equation:

$$W_v = C_v \pi \rho_m D_m g (H_v + 0.8 D_m) t \times 10^{-3} \quad (13.75)$$

where  $W_v$  = total weight of the shell, excluding internal fittings, such as plates,  $N$ ,

$C_v$  = a factor to account for the weight of nozzles, manways, internal supports, etc; which can be taken as

= 1.08 for vessels with only a few internal fittings,

= 1.15 for distillation columns, or similar vessels, with several manways, and with plate support rings, or equivalent fittings,

$H_v$  = height, or length, between tangent lines (the length of the cylindrical section), m,

$g$  = gravitational acceleration,  $9.81 \text{ m/s}^2$ ,

$t$  = wall thickness, mm

$\rho_m$  = density of vessel material,  $\text{kg/m}^3$ ,

$D_m$  = mean diameter of vessel =  $(D_i + t \times 10^{-3})$ , m.

For a steel vessel, equation 13.75 reduces to:

$$W_v = 240 C_v D_m (H_v + 0.8 D_m) t \quad (13.76)$$

The following values can be used as a rough guide to the weight of fittings; see Nelson (1963):

- (a) caged ladders, steel, 360 N/m length,
- (b) plain ladders, steel, 150 N/m length,
- (c) platforms, steel, for vertical columns,  $1.7 \text{ kN/m}^2$  area,
- (d) contacting plates, steel, including typical liquid loading,  $1.2 \text{ kN/m}^2$  plate area.

Typical values for the density of insulating materials are (all  $\text{kg/m}^3$ ):

Foam glass	150
Mineral wool	130
Fibreglass	100
Calcium silicate	200

These densities should be doubled to allow for attachment fittings, sealing, and moisture absorption.

### 13.8.2. Wind loads (tall vessels)

Wind loading will only be important on tall columns installed in the open. Columns and chimney-stacks are usually free standing, mounted on skirt supports, and not attached to structural steel work. Under these conditions the vessel under wind loading acts as a cantilever beam, Figure 13.19. For a uniformly loaded cantilever the bending moment at any plane is given by:

$$M_x = \frac{wx^2}{2} \quad (13.77)$$

where  $x$  is the distance measured from the free end and  $w$  the load per unit length (Newtons per metre run).

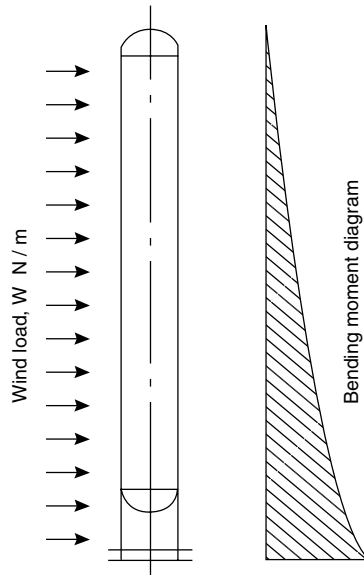


Figure 13.19. Wind loading on a tall column

So the bending moment, and hence the bending stress, will vary parabolically from zero at the top of the column to a maximum value at the base. For tall columns the bending stress due to wind loading will often be greater than direct stress due to pressure, and will determine the plate thickness required. The most economical design will be one in which the plate thickness is progressively increased from the top to the base of the column. The thickness at the top being sufficient for the pressure load, and that at the base sufficient for the pressure plus the maximum bending moment.

Any local increase in the column area presented to the wind will give rise to a local, concentrated, load, Figure 13.20. The bending moment at the column base caused by a concentrated load is given by:

$$M_p = F_p H_p \quad (13.78)$$

where  $F_p$  = local, concentrated, load,

$H_p$  = the height of the concentrated load above the column base.

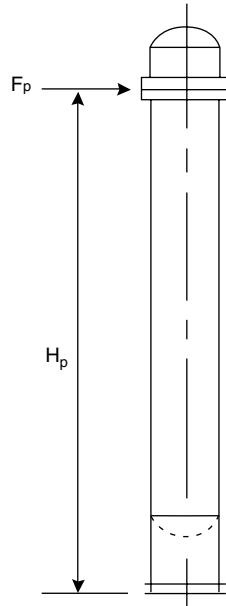


Figure 13.20. Local wind loading

### ***Dynamic wind pressure***

The load imposed on any structure by the action of the wind will depend on the shape of the structure and the wind velocity.

$$P_w = \frac{1}{2} C_d \rho_a u_w^2 \quad (13.79)$$

where  $P_w$  = wind pressure (load per unit area),

$C_d$  = drag coefficient (shape factor),

$\rho_a$  = density of air,

$u_w$  = wind velocity.

The drag coefficient is a function of the shape of the structure and the wind velocity (Reynolds number).

For a smooth cylindrical column or stack the following semi-empirical equation can be used to estimate the wind pressure:

$$P_w = 0.05 u_w^2 \quad (13.79a)$$

where  $P_w$  = wind pressure,  $\text{N/m}^2$ ,

$u_w$  = wind speed,  $\text{km/h}$ .

If the column outline is broken up by attachments, such as ladders or pipe work, the factor of 0.05 in equation 13.79a should be increased to 0.07, to allow for the increased drag.

A column must be designed to withstand the highest wind speed that is likely to be encountered at the site during the life of the plant. The probability of a given wind speed occurring can be predicted by studying meteorological records for the site location.

Data and design methods for wind loading are given in the Engineering Sciences Data Unit (ESDU) Wind Engineering Series ([www.ihsedsu.com](http://www.ihsedsu.com)).

Design loadings for locations in the United States are given by Moss (2003), Megyesy (2001) and Escoe (1994).

A wind speed of 160 km/h (100 mph) can be used for preliminary design studies; equivalent to a wind pressure of 1280 N/m<sup>2</sup> (25 lb/ft<sup>2</sup>).

At any site, the wind velocity near the ground will be lower than that higher up (due to the boundary layer), and in some design methods a lower wind pressure is used at heights below about 20 m; typically taken as one-half of the pressure above this height.

The loading per unit length of the column can be obtained from the wind pressure by multiplying by the effective column diameter: the outside diameter plus an allowance for the thermal insulation and attachments, such as pipes and ladders.

$$F_w = P_w D_{\text{eff}} \quad (13.80)$$

An allowance of 0.4 m should be added for a caged ladder. The calculation of the wind load on a tall column, and the induced bending stresses, is illustrated in Example 13.3. Further examples of the design of tall columns are given by Brownell (1963), Henry (1973), Bednar (1990), Escoe (1994) and Jawad and Farr (1989).

### ***Deflection of tall columns***

Tall columns sway in the wind. The allowable deflection will normally be specified as less than 150 mm per 30 metres of height (6 in. per 100 ft).

For a column with a uniform cross-section, the deflection can be calculated using the formula for the deflection of a uniformly loaded cantilever. A method for calculating the deflection of a column where the wall thickness is not constant is given by Tang (1968).

### ***Wind-induced vibrations***

Vortex shedding from tall thin columns and stacks can induce vibrations which, if the frequency of shedding of eddies matches the natural frequency of the column, can be severe enough to cause premature failure of the vessel by fatigue. The effect of vortex shedding should be investigated for free standing columns with height to diameter ratios greater than 10. Methods for estimating the natural frequency of columns are given by Freese (1959) and DeGhetto and Long (1966).

Helical strakes (strips) are fitted to the tops of tall smooth chimneys to change the pattern of vortex shedding and so prevent resonant oscillation. The same effect will be achieved on a tall column by distributing any attachments (ladders, pipes and platforms) around the column.

### **13.8.3. Earthquake loading**

The movement of the earth's surface during an earthquake produces horizontal shear forces on tall self-supported vessels, the magnitude of which increases from the base upward. The total shear force on the vessel will be given by:

$$F_s = a_e \left( \frac{W}{g} \right) \quad (13.81)$$



where  $a_e$  = the acceleration of the vessel due to the earthquake,  
 $g$  = the acceleration due to gravity,  
 $W$  = total weight of the vessel.

The term  $(a_e/g)$  is called the seismic constant  $C_e$ , and is a function of the natural period of vibration of the vessel and the severity of the earthquake. Values of the seismic constant have been determined empirically from studies of the damage caused by earthquakes, and are available for those geographical locations which are subject to earthquake activity. Values for sites in the United States, and procedures for determining the stresses induced in tall columns are given by Megyesy (2001), Escoe (1994) and Moss (2003).

A seismic stress analysis is not made as a routine procedure in the design of vessels for sites in the United Kingdom, except for nuclear installations, as the probability of an earthquake occurring of sufficient severity to cause significant damage is negligible. However, the possibility of earthquake damage may be considered if the site is a Major Hazards installation, see Chapter 9, Section 9.9.

#### 13.8.4. Eccentric loads (tall vessels)

Ancillary equipment attached to a tall vessel will subject the vessel to a bending moment if the centre of gravity of the equipment does not coincide with the centre line of the vessel (Figure 13.21). The moment produced by small fittings, such as ladders, pipes and manways, will be small and can be neglected. That produced by heavy equipment, such as reflux condensers and side platforms, can be significant and should be considered. The moment is given by:

$$M_e = W_e L_o \quad (13.82)$$

where  $W_e$  = dead weight of the equipment,

$L_o$  = distance between the centre of gravity of the equipment and the column centre line.

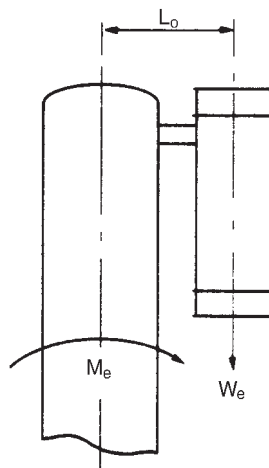


Figure 13.21. Bending moment due to offset equipment

### 13.8.5. Torque

Any horizontal force imposed on the vessel by ancillary equipment, the line of thrust of which does not pass through the centre line of the vessel, will produce a torque on the vessel. Such loads can arise through wind pressure on piping and other attachments. However, the torque will normally be small and usually can be disregarded. The pipe work and the connections for any ancillary equipment will be designed so as not to impose a significant load on the vessel.

#### Example 13.3

Make a preliminary estimate of the plate thickness required for the distillation column specified below:

Height, between tangent lines	50 m
Diameter	2 m
Skirt support, height	3 m
100 sieve plates, equally spaced	
Insulation, mineral wool	75 mm thick
Material of construction, stainless steel, design stress 135 N/mm <sup>2</sup> at design temperature 200°C	
Operating pressure 10 bar (absolute)	
Vessel to be fully radiographed (joint factor 1).	

#### Solution

Design pressure; take as 10 per cent above operating pressure

$$= (10 - 1) \times 1.1 = 9.9 \text{ bar, say } 10 \text{ bar}$$

$$= 1.0 \text{ N/mm}^2$$

Minimum thickness required for pressure loading

$$= \frac{1 \times 2 \times 10^3}{2 \times 135 - 1} = 7.4 \text{ mm} \quad (13.39)$$

A much thicker wall will be needed at the column base to withstand the wind and dead weight loads.

As a first trial, divide the column into five sections (courses), with the thickness increasing by 2 mm per section. Try 10, 12, 14, 16, 18 mm.

#### ***Dead weight of vessel***

Though equation 13.76 only applies strictly to vessels with uniform thickness, it can be used to get a rough estimate of the weight of this vessel by using the average thickness in the equation, 14 mm.

Take  $C_v = 1.15$ , vessel with plates,

$$D_m = 2 + 14 \times 10^{-3} = 2.014 \text{ m,}$$

$$\begin{aligned}
 H_v &= 50 \text{ m,} \\
 t &= 14 \text{ mm} \\
 W_v &= 240 \times 1.15 \times 2.014(50 + 0.8 \times 2.014)14 \\
 &= 401643 \text{ N} \\
 &= 402 \text{ kN}
 \end{aligned}
 \tag{13.76}$$

Weight of plates:

$$\begin{aligned}
 \text{plate area} &= \pi/4 \times 2^2 = 3.14 \text{ m}^2 \\
 \text{weight of a plate (see page 761)} &= 1.2 \times 3.14 = 3.8 \text{ kN} \\
 100 \text{ plates} &= 100 \times 3.8 = 380 \text{ kN}
 \end{aligned}$$

Weight of insulation:

$$\begin{aligned}
 \text{mineral wool density} &= 130 \text{ kg/m}^3 \\
 \text{approximate volume of insulation} &= \pi \times 2 \times 50 \times 75 \times 10^{-3} \\
 &= 23.6 \text{ m}^3 \\
 \text{weight} &= 23.6 \times 130 \times 9.81 = 30,049 \text{ N} \\
 \text{double this to allow for fittings, etc.} &= 60 \text{ kN}
 \end{aligned}$$

Total weight:

shell	402
plates	380
insulation	60
	842 kN

### **Wind loading**

Take dynamic wind pressure as 1280 N/m<sup>2</sup>.

$$\begin{aligned}
 \text{Mean diameter, including insulation} &= 2 + 2(14 + 75) \times 10^{-3} \\
 &= 2.18 \text{ m}
 \end{aligned}$$

$$\text{Loading (per linear metre) } F_w = 1280 \times 2.18 = 2790 \text{ N/m} \tag{13.80}$$

Bending moment at bottom tangent line:

$$M_x = \frac{2790}{2} \times 50^2 = 3,487,500 \text{ Nm} \tag{13.77}$$

### **Analysis of stresses**

At bottom tangent line

Pressure stresses:

$$\sigma_L = \frac{1.0 \times 2 \times 10^3}{4 \times 18} = 27.8 \text{ N/mm}^2 \tag{13.64}$$

$$\sigma_h = \frac{1 \times 2 \times 10^3}{2 \times 18} = 55.6 \text{ N/mm}^2 \tag{13.63}$$

Dead weight stress:

$$\begin{aligned}\sigma_w &= \frac{W_v}{\pi(D_i + t)t} = \frac{842 \times 10^3}{\pi(2000 + 18)18} \\ &= 7.4 \text{ N/mm}^2 \text{ (compressive)}\end{aligned}\quad (13.65)$$

Bending stresses:

$$\begin{aligned}D_o &= 2000 + 2 \times 18 = 2036 \text{ mm} \\ I_v &= \frac{\pi}{64}(2036^4 - 2000^4) = 5.81 \times 10^{10} \text{ mm}^4\end{aligned}\quad (13.67)$$

$$\begin{aligned}\sigma_b &= \pm \frac{3,487,500 \times 10^3}{5.81 \times 10^{10}} \left( \frac{2000}{2} + 18 \right) \\ &= \pm 61.1 \text{ N/mm}^2\end{aligned}\quad (13.66)$$

The resultant longitudinal stress is:

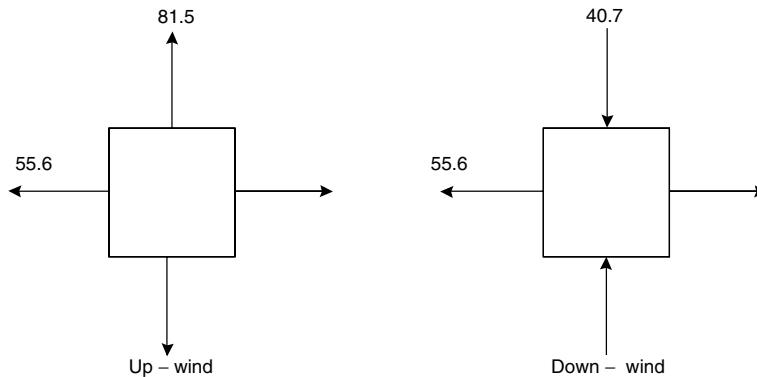
$$\sigma_z = \sigma_L + \sigma_w \pm \sigma_b$$

$\sigma_w$  is compressive and therefore negative.

$$\sigma_z \text{ (upwind)} = 27.8 - 7.4 + 61.1 = +81.5 \text{ N/mm}^2.$$

$$\sigma_z \text{ (downwind)} = 27.8 - 7.4 - 61.1 = -40.7 \text{ N/mm}^2.$$

As there is no torsional shear stress, the principal stresses will be  $\sigma_z$  and  $\sigma_h$ . The radial stress is negligible,  $\simeq (P_i/2) = 0.5 \text{ N/mm}^2$ .



The greatest difference between the principal stresses will be on the down-wind side

$$(55.6 - (-40.7)) = \underline{\underline{96.5 \text{ N/mm}^2}},$$

well below the maximum allowable design stress

### **Check elastic stability (buckling)**

Critical buckling stress:

$$\sigma_c = 2 \times 10^4 \left( \frac{18}{2036} \right) = \underline{\underline{176.8 \text{ N/mm}^2}}\quad (13.74)$$

The maximum compressive stress will occur when the vessel is not under pressure =  $7.4 + 61.1 = 68.5$ , well below the critical buckling stress.

So design is satisfactory. Could reduce the plate thickness and recalculate.

### 13.9. VESSEL SUPPORTS

The method used to support a vessel will depend on the size, shape, and weight of the vessel; the design temperature and pressure; the vessel location and arrangement; and the internal and external fittings and attachments. Horizontal vessels are usually mounted on two saddle supports; Figure 13.22. Skirt supports are used for tall, vertical columns; Figure 13.23. Brackets, or lugs, are used for all types of vessel; Figure 13.24. The supports must be designed to carry the weight of the vessel and contents, and any superimposed loads, such as wind loads. Supports will impose localised loads on the vessel wall, and the design must be checked to ensure that the resulting stress concentrations are below the maximum allowable design stress. Supports should be designed to allow easy access to the vessel and fittings for inspection and maintenance.

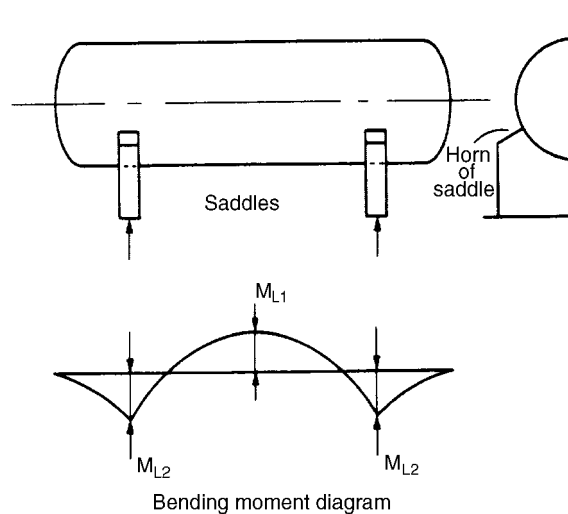


Figure 13.22. Horizontal cylindrical vessel on saddle supports

#### 13.9.1. Saddle supports

Though saddles are the most commonly used support for horizontal cylindrical vessels, legs can be used for small vessels. A horizontal vessel will normally be supported at two cross-sections; if more than two saddles are used the distribution of the loading is uncertain.

A vessel supported on two saddles can be considered as a simply supported beam, with an essentially uniform load, and the distribution of longitudinal axial bending moment will be as shown in Figure 13.22. Maxima occur at the supports and at mid-span. The

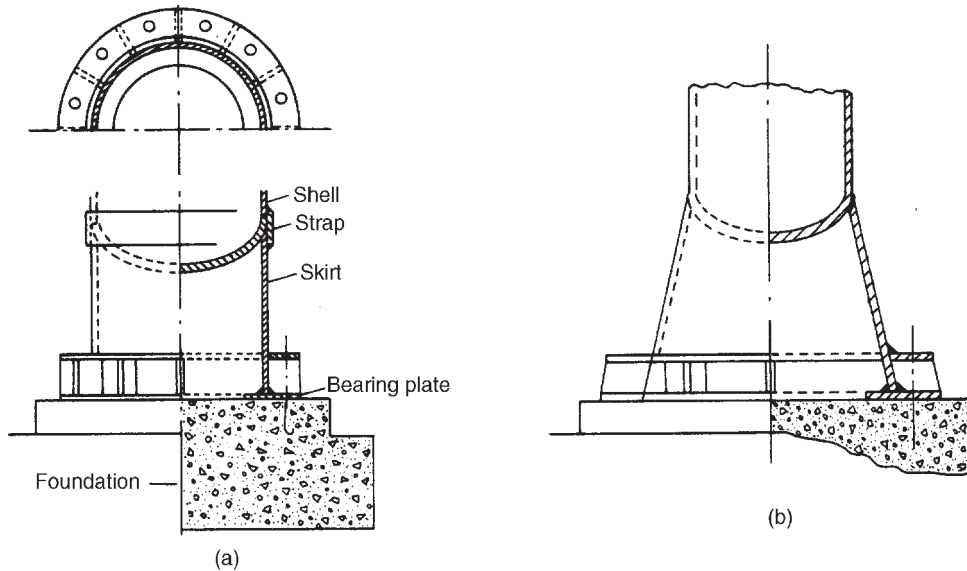


Figure 13.23. Typical skirt-support designs (a) Straight skirt (b) Conical skirt

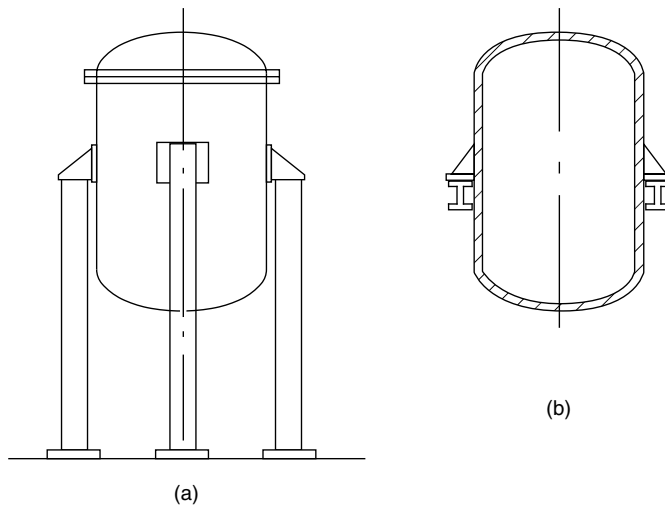


Figure 13.24. Bracket supports (a) Supported on legs (b) Supported from steel-work

theoretical optimum position of the supports to give the least maximum bending moment will be the position at which the maxima at the supports and at mid-span are equal in magnitude. For a uniformly loaded beam the position will be at 21 per cent of the span, in from each end. The saddle supports for a vessel will usually be located nearer the ends than this value, to make use of the stiffening effect of the ends.

### ***Stress in the vessel wall***

The longitudinal bending stress at the mid-span of the vessel is given by:

$$\sigma_{b1} = \frac{M_{L1}}{I_h} \times \frac{D}{2} \simeq \frac{4M_{L1}}{\pi D^2 t} \quad (13.83)$$

where  $M_{L1}$  = longitudinal bending stress at the mid-span,

$I_h$  = second moment of area of the shell,

$D$  = shell diameter,

$t$  = shell thickness.

The resultant axial stress due to bending and pressure will be given by:

$$\sigma_z = \frac{PD}{4t} \pm \frac{4M_{L1}}{\pi D^2 t} \quad (13.84)$$

The magnitude of the longitudinal bending stress at the supports will depend on the local stiffness of the shell; if the shell does not remain circular under load a portion of the upper part of the cross-section is ineffective against longitudinal bending; see Figure 13.25. The stress is given by:

$$\sigma_{b2} = \frac{4M_{L2}}{C_h \pi D^2 t} \quad (13.85)$$

where  $M_{L2}$  = longitudinal bending moment at the supports,

$C_h$  = an empirical constant; varying from 1.0 for a completely stiff shell to about 0.1 for a thin, unstiffened, shell.

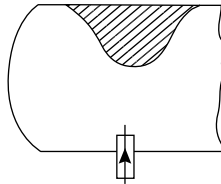


Figure 13.25. Saddle supports: shaded area is ineffective against longitudinal bending in an unstiffened shell

The ends of the vessels will stiffen the shell if the position of the saddles is less than  $D/4$  from the ends. Ring stiffeners, located at the supports, are used to stiffen the shells of long thin vessels. The rings may be fitted inside or outside the vessel.

In addition to the longitudinal bending stress, a vessel supported on saddles will be subjected to tangential shear stresses, which transfer the load from the unsupported sections of the vessel to the supports; and to circumferential bending stresses. All these stresses need to be considered in the design of large, thin-walled, vessels, to ensure that the resultant stress does not exceed the maximum allowable design stress or the critical buckling stress for the material. A detailed stress analysis is beyond the scope of this

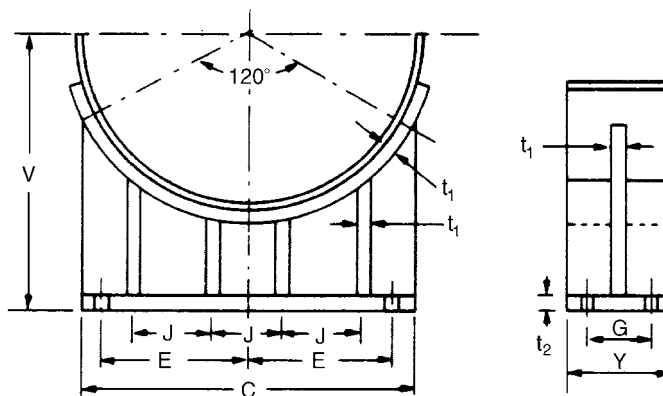
book. A complete analysis of the stress induced in the shell by the supports is given by Zick (1951). Zick's method forms the basis of the design methods given in the national codes and standards. The method is also given by Brownell and Young (1959), Escoe (1994) and Megyesy (2001).

### Design of saddles

The saddles must be designed to withstand the load imposed by the weight of the vessel and contents. They are constructed of bricks or concrete, or are fabricated from steel plate. The contact angle should not be less than  $120^\circ$ , and will not normally be greater than  $150^\circ$ . Wear plates are often welded to the shell wall to reinforce the wall over the area of contact with the saddle.

The dimensions of typical "standard" saddle designs are given in Figure 13.26. To take up any thermal expansion of the vessel, such as that in heat exchangers, the anchor bolt holes in one saddle can be slotted.

Procedures for the design of saddle supports are given by Brownell and Young (1959), Megyesy (2001), Escoe (1994) and Moss (2003).



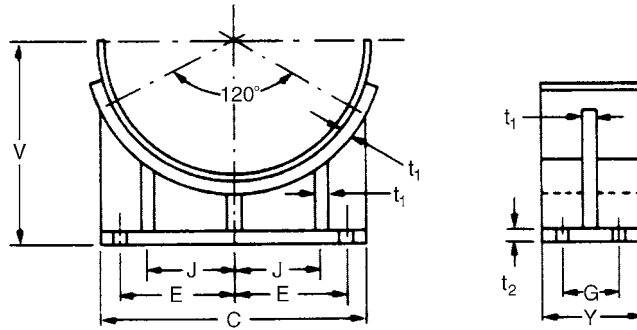
Vessel diam. (m)	Maximum weight (kN)	Dimensions (m)						mm			
		V	Y	C	E	J	G	t <sub>2</sub>	t <sub>1</sub>	Bolt diam.	Bolt holes
0.6	35	0.48	0.15	0.55	0.24	0.190	0.095	6	5	20	25
0.8	50	0.58	0.15	0.70	0.29	0.225	0.095	8	5	20	25
0.9	65	0.63	0.15	0.81	0.34	0.275	0.095	10	6	20	25
1.0	90	0.68	0.15	0.91	0.39	0.310	0.095	11	8	20	25
1.2	180	0.78	0.20	1.09	0.45	0.360	0.140	12	10	24	30

All contacting edges fillet welded

(a)

Figure 13.26. Standard steel saddles (adapted from Bhattacharyya, 1976). (a) for vessels up to 1.2 m





Vessel diam. (m)	Maximum weight (kN)	Dimensions (m)						mm			
		V	Y	C	E	J	G	$t_2$	$t_1$	Bolt diam.	Bolt holes
1.4	230	0.88	0.20	1.24	0.53	0.305	0.140	12	10	24	30
1.6	330	0.98	0.20	1.41	0.62	0.350	0.140	12	10	24	30
1.8	380	1.08	0.20	1.59	0.71	0.405	0.140	12	10	24	30
2.0	460	1.18	0.20	1.77	0.80	0.450	0.140	12	10	24	30
2.2	750	1.28	0.225	1.95	0.89	0.520	0.150	16	12	24	30
2.4	900	1.38	0.225	2.13	0.98	0.565	0.150	16	12	27	33
2.6	1000	1.48	0.225	2.30	1.03	0.590	0.150	16	12	27	33
2.8	1350	1.58	0.25	2.50	1.10	0.625	0.150	16	12	27	33
3.0	1750	1.68	0.25	2.64	1.18	0.665	0.150	16	12	27	33
3.2	2000	1.78	0.25	2.82	1.26	0.730	0.150	16	12	27	33
3.6	2500	1.98	0.25	3.20	1.40	0.815	0.150	16	12	27	33

All contacting edges fillet welded

(b)

Figure 13.26. (b) for vessels greater than 1.2 m

### 13.9.2. Skirt supports

A skirt support consists of a cylindrical or conical shell welded to the base of the vessel. A flange at the bottom of the skirt transmits the load to the foundations. Typical designs are shown in Figure 13.23. Openings must be provided in the skirt for access and for any connecting pipes; the openings are normally reinforced. The skirt may be welded to the bottom head of the vessel. Figure 13.27a; or welded flush with the shell, Figure 13.27b; or welded to the outside of the vessel shell, Figure 13.27c. The arrangement shown in Figure 13.27b is usually preferred.

Skirt supports are recommended for vertical vessels as they do not impose concentrated loads on the vessel shell; they are particularly suitable for use with tall columns subject to wind loading.

#### Skirt thickness

The skirt thickness must be sufficient to withstand the dead-weight loads and bending moments imposed on it by the vessel; it will not be under the vessel pressure.

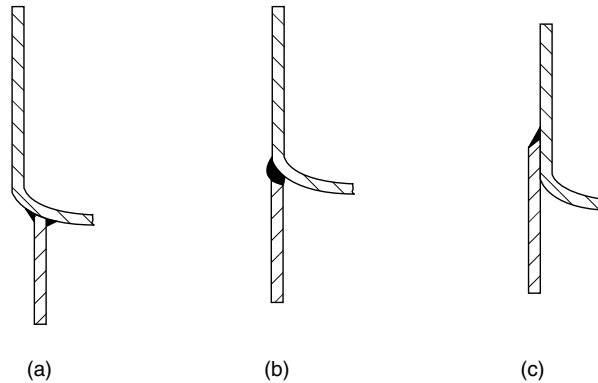


Figure 13.27. Skirt-support welds

The resultant stresses in the skirt will be:

$$\sigma_s \text{ (tensile)} = \sigma_{bs} - \sigma_{ws} \quad (13.86)$$

and

$$\sigma_s \text{ (compressive)} = \sigma_{bs} + \sigma_{ws} \quad (13.87)$$

where  $\sigma_{bs}$  = bending stress in the skirt

$$= \frac{4M_s}{\pi(D_s + t_s)t_s D_s}, \quad (13.88)$$

$\sigma_{ws}$  = the dead weight stress in the skirt,

$$= \frac{W}{\pi(D_s + t_s)t_s} \quad (13.89)$$

where  $M_s$  = maximum bending moment, evaluated at the base of the skirt (due to wind, seismic and eccentric loads, see Section 13.8),

$W$  = total weight of the vessel and contents (see Section 13.8),

$D_s$  = inside diameter of the skirt, at the base,

$t_s$  = skirt thickness.

The skirt thickness should be such that under the worst combination of wind and dead-weight loading the following design criteria are not exceeded:

$$\sigma_s \text{ (tensile)} \neq f_s J \sin \theta_s \quad (13.90)$$

$$\sigma_s \text{ (compressive)} \neq 0.125E \left( \frac{t_s}{D_s} \right) \sin \theta_s \quad (13.91)$$

where  $f_s$  = maximum allowable design stress for the skirt material, normally taken at ambient temperature, 20°C,

- $J$  = weld joint factor, if applicable,  
 $\theta_s$  = base angle of a conical skirt, normally  $80^\circ$  to  $90^\circ$ .

The minimum thickness should be not less than 6 mm.

Where the vessel wall will be at a significantly higher temperature than the skirt, discontinuity stresses will be set up due to differences in thermal expansion. Methods for calculating the thermal stresses in skirt supports are given by Weil and Murphy (1960) and Bergman (1963).

### **Base ring and anchor bolt design**

The loads carried by the skirt are transmitted to the foundation slab by the skirt base ring (bearing plate). The moment produced by wind and other lateral loads will tend to overturn the vessel; this will be opposed by the couple set up by the weight of the vessel and the tensile load in the anchor bolts. A variety of base ring designs is used with skirt supports. The simplest types, suitable for small vessels, are the rolled angle and plain flange rings shown in Figure 13.28*a* and *b*. For larger columns a double ring stiffened by gussets, Figure 13.18*c*, or chair supports, Figure 13.30, are used. Design methods for base rings, and methods for sizing the anchor bolts, are given by Brownell and Young (1959). For preliminary design, the short-cut method and nomographs given by Scheiman (1963) can be used. Scheiman's method is based on a more detailed procedure for the design of base rings and foundations for columns and stacks given by Marshall (1958). Scheiman's method is outlined below and illustrated in Example 13.4.

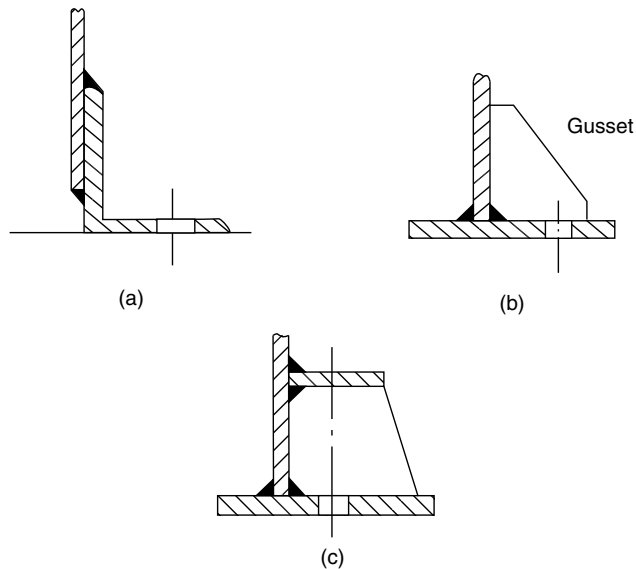


Figure 13.28. Flange ring designs (a) Rolled-angle (b) Single plate with gusset (c) Double plate with gusset

The anchor bolts are assumed to share the overturning load equally, and the bolt area required is given by:

$$A_b = \frac{1}{N_b f_b} \left[ \frac{4M_s}{D_b} - W \right] \quad (13.92)$$

where  $A_b$  = area of one bolt at the root of the thread, mm<sup>2</sup>,

$N_b$  = number of bolts,

$f_b$  = maximum allowable bolt stress, N/mm<sup>2</sup>;  
typical design value 125 N/mm<sup>2</sup> (18,000 psi),

$M_s$  = bending (overturning) moment at the base, Nm,

$W$  = weight of the vessel, N,

$D_b$  = bolt circle diameter, m.

Scheiman gives the following guide rules which can be used for the selection of the anchor bolts:

1. Bolts smaller than 25 mm (1 in.) diameter should not be used.
2. Minimum number of bolts 8.
3. Use multiples of 4 bolts.
4. Bolt pitch should not be less than 600 mm (2 ft).

If the minimum bolt pitch cannot be accommodated with a cylindrical skirt, a conical skirt should be used.

The base ring must be sufficiently wide to distribute the load to the foundation. The total compressive load on the base ring is given by:

$$F_b = \left[ \frac{4M_s}{\pi D_s^2} + \frac{W}{\pi D_s} \right] \quad (13.93)$$

where  $F_b$  = the compressive load on the base ring, Newtons per linear metre,

$D_s$  = skirt diameter, m.

The minimum width of the base ring is given by:

$$L_b = \frac{F_b}{f_c} \times \frac{1}{10^3} \quad (13.94)$$

where  $L_b$  = base ring width, mm (Figure 13.29),

$f_c$  = the maximum allowable bearing pressure on the concrete foundation pad,  
which will depend on the mix used, and will typically range from 3.5 to  
7 N/mm<sup>2</sup> (500 to 1000 psi).

The required thickness for the base ring is found by treating the ring as a cantilever beam.

The minimum thickness is given by:

$$t_b = L_r \sqrt{\frac{3f'_c}{f_r}} \quad (13.95)$$

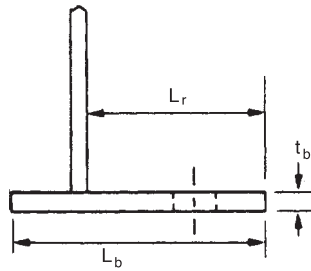
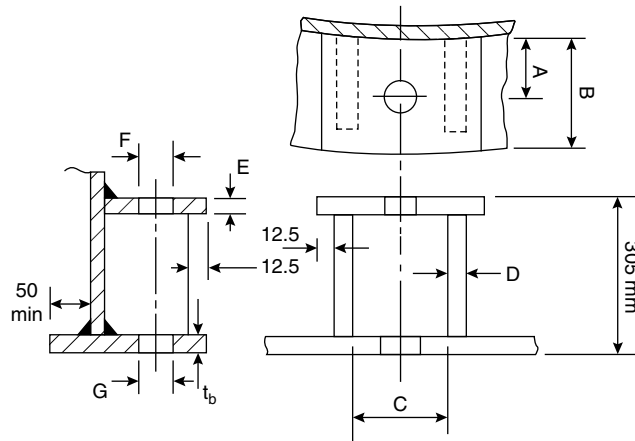


Figure 13.29. Flange ring dimensions



All contacting edges fillet welded

Dimensions mm

Bolt size	Root area	A	B	C	D	E	F	G
M24	353	45	76	64	13	19	30	36
M30	561	50	76	64	13	25	36	42
M36	817	57	102	76	16	32	42	48
M42	1120	60	102	76	16	32	48	54
M48	1470	67	127	89	19	38	54	60
M56	2030	75	150	102	25	45	60	66
M64	2680	83	152	102	25	50	70	76
70	—	89	178	127	32	64	76	83
76	—	95	178	127	32	64	83	89

Bolt size = Nominal dia. (BS 4190: 1967)

Figure 13.30. Anchor bolt chair design

where  $L_r$  = the distance from the edge of the skirt to the outer edge of the ring, mm;

Figure 13.29,

$t_b$  = base ring thickness, mm,

$f'_c$  = actual bearing pressure on base,  $\text{N/mm}^2$ ,

$f_r$  = allowable design stress in the ring material, typically  $140 \text{ N/mm}^2$ .

Standard designs will normally be used for the bolting chairs. The design shown in Figure 13.30 has been adapted from that given by Scheiman.

### Example 13.4

Design a skirt support for the column specified in Example 13.3.

### Solution

Try a straight cylindrical skirt ( $\theta_s = 90^\circ$ ) of plain carbon steel, design stress 135 N/mm<sup>2</sup> and Young's modulus 200,000 N/mm<sup>2</sup> at ambient temperature.

The maximum dead weight load on the skirt will occur when the vessel is full of water.

$$\begin{aligned}\text{Approximate weight} &= \left(\frac{\pi}{4} \times 2^2 \times 50\right) 1000 \times 9.81 \\ &= 1,540,951 \text{ N} \\ &= 1541 \text{ kN}\end{aligned}$$

Weight of vessel, from Example 13.3 = 842 kN

Total weight = 1541 + 842 = 2383 kN

Wind loading, from Example 13.4 = 2.79 kN/m

$$\begin{aligned}\text{Bending moment at base of skirt} &= 2.79 \times \frac{53^2}{2} \\ &= 3919 \text{ kNm}\end{aligned}\tag{13.77}$$

As a first trial, take the skirt thickness as the same as that of the bottom section of the vessel, 18 mm.

$$\begin{aligned}\sigma_{bs} &= \frac{4 \times 3919 \times 10^3 \times 10^3}{\pi(2000 + 18)2000 \times 18} \\ &= 68.7 \text{ N/mm}^2\end{aligned}\tag{13.88}$$

$$\sigma_{ws} \text{ (test)} = \frac{1543 \times 10^3}{\pi(2000 + 18)18} = 13.5 \text{ N/mm}^2\tag{13.89}$$

$$\sigma_{ws} \text{ (operating)} = \frac{842 \times 10^3}{\pi(2000 + 18)18} = 7.4 \text{ N/mm}^2\tag{13.89}$$

*Note:* the “test” condition is with the vessel full of water for the hydraulic test. In estimating total weight, the weight of liquid on the plates has been counted twice. The weight has not been adjusted to allow for this as the error is small, and on the “safe side”.

$$\text{Maximum } \hat{\sigma}_s \text{ (compressive)} = 68.7 + 13.5 = 82.2 \text{ N/mm}^2\tag{13.87}$$

$$\text{Maximum } \hat{\sigma}_s \text{ (tensile)} = 68.7 - 7.4 = 61.3 \text{ N/mm}^2\tag{13.86}$$

Take the joint factor  $J$  as 0.85.

Criteria for design:

$$\hat{\sigma}_s \text{ (tensile)} \neq f_s J \sin \theta \quad (13.90)$$

$$61.3 \neq 0.85 \times 135 \sin 90$$

$$61.3 \neq 115$$

$$\hat{\sigma}_s \text{ (compressive)} \neq 0.125E \left( \frac{t_s}{D_s} \right) \sin \theta \quad (13.91)$$

$$82.2 \neq 0.125 \times 200,000 \left( \frac{18}{2000} \right) \sin 90$$

$$82.2 \neq 225$$

Both criteria are satisfied, add 2 mm for corrosion, gives a design thickness of 20 mm

### **Base ring and anchor bolts**

Approximate pitch circle dia., say, 2.2 m

Circumference of bolt circle =  $2200\pi$

Number of bolts required, at minimum recommended bolt spacing

$$= \frac{2200\pi}{600} = 11.5$$

Closest multiple of 4 = 12 bolts

Take bolt design stress =  $125 \text{ N/mm}^2$

$M_s = 3919 \text{ kN m}$

Take  $W =$  operating value =  $842 \text{ kN}$ .

$$A_b = \frac{1}{12 \times 125} \left[ \frac{4 \times 3919 \times 10^3}{2.2} - 842 \times 10^3 \right] \quad (13.92)$$

$$= 4190 \text{ mm}^2$$

$$\text{Bolt root dia.} = \sqrt{\frac{4190 \times 4}{\pi}} = 73 \text{ mm, looks too large.}$$

Total compressive load on the base ring per unit length

$$F_b = \left[ \frac{4 \times 3919 \times 10^3}{\pi \times 2.0^2} + \frac{842 \times 10^3}{\pi \times 2.0} \right] \quad (13.93)$$

$$= 1381 \times 10^3 \text{ N/m}$$

Taking the bearing pressure as  $5 \text{ N/mm}^2$

$$L_b = \frac{1381 \times 10^3}{5 \times 10^3} = 276 \text{ mm} \quad (13.94)$$

Rather large—consider a flared skirt.

Take the skirt bottom dia. as 3 m

$$\text{Skirt base angle } \theta_s = \tan^{-1} \frac{3}{\frac{1}{2}(3-2)} = 80.5^\circ$$

Keep the skirt thickness the same as that calculated for the cylindrical skirt. Highest stresses will occur at the top of the skirt; where the values will be close to those calculated for the cylindrical skirt.  $\sin 80.5^\circ = 0.99$ , so this term has little effect on the design criteria.

Assume bolt circle dia. = 3.2 m.

Take number of bolts as 16.

$$\text{Bolt spacing} = \frac{\pi \times 3.2 \times 10^3}{16} = 628 \text{ mm satisfactory.}$$

$$\begin{aligned} A_b &= \frac{1}{16 \times 125} \left[ \frac{4 \times 3919 \times 10^3}{3.2} - 842 \times 10^3 \right] \\ &= \underline{\underline{2029 \text{ mm}^2}} \end{aligned}$$

Use M56 bolts (BS 4190:1967) root area = 2030 mm<sup>2</sup>,

$$\begin{aligned} F_b &= \left[ \frac{4 \times 3919 \times 10^3}{\pi \times 3.0^2} + \frac{842 \times 10^3}{\pi \times 3.0} \right] \\ &= 644 \text{ kN/m.} \\ L_b &= \frac{644 \times 10^3}{5 \times 10^3} = 129 \text{ mm} \end{aligned}$$

This is the minimum width required; actual width will depend on the chair design.

Actual width required (Figure 13.30):

$$\begin{aligned} &= L_r + t_s + 50 \text{ mm} \\ &= 150 + 20 + 50 = \underline{\underline{220 \text{ mm}}} \end{aligned}$$

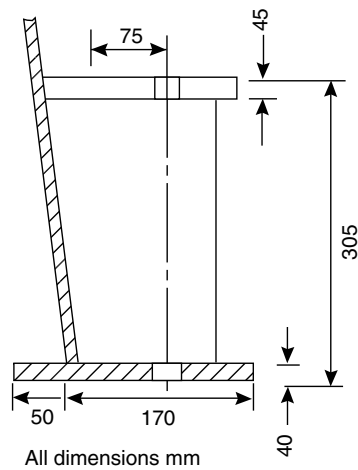
Actual bearing pressure on concrete foundation:

$$\begin{aligned} f'_c &= \frac{644 \times 10^3}{220 \times 10^3} = 2.93 \text{ N/mm}^2 \\ t_b &= 150 \sqrt{\frac{3 \times 2.93}{140}} = 37.6 \text{ mm} \\ &\text{round off to } \underline{\underline{40 \text{ mm}}} \end{aligned} \quad (13.95)$$

Chair dimensions from Figure 13.30 for bolt size M56.

Skirt to be welded flush with outer diameter of column shell.





### 13.9.3. Bracket supports

Brackets, or lugs, can be used to support vertical vessels. The bracket may rest on the building structural steel work, or the vessel may be supported on legs; Figure 13.24.

The main load carried by the brackets will be the weight of the vessel and contents; in addition the bracket must be designed to resist the load due to any bending moment due to wind, or other loads. If the bending moment is likely to be significant skirt supports should be considered in preference to bracket supports.

As the reaction on the bracket is eccentric, Figure 13.31, the bracket will impose a bending moment on the vessel wall. The point of support, at which the reaction acts, should be made as close to the vessel wall as possible; allowing for the thickness of any insulation. Methods for estimating the magnitude of the stresses induced in the vessel

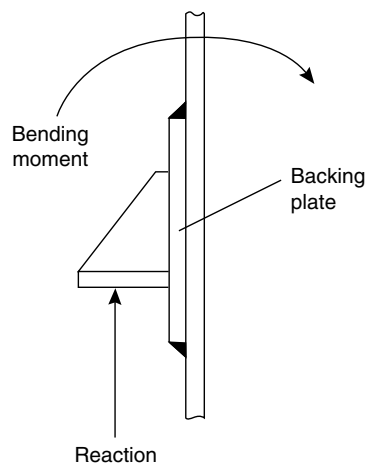


Figure 13.31. Loads on a bracket support

wall by bracket supports are given by Brownell and Young (1959) and by Wolosewick (1951). Backing plates are often used to carry the bending loads.

The brackets, and supporting steel work, can be designed using the usual methods for structural steelwork. Suitable methods are given by Bednar (1986) and Moss (2003).

A quick method for sizing vessel reinforcing rings (backing plates) for bracket supports is given by Mahajan (1977).

Typical bracket designs are shown in Figures 13.32a and b. The loads which steel brackets with these proportions will support are given by the following formula:

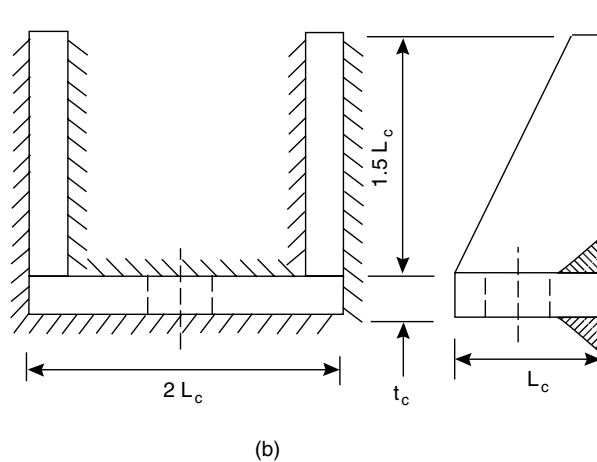
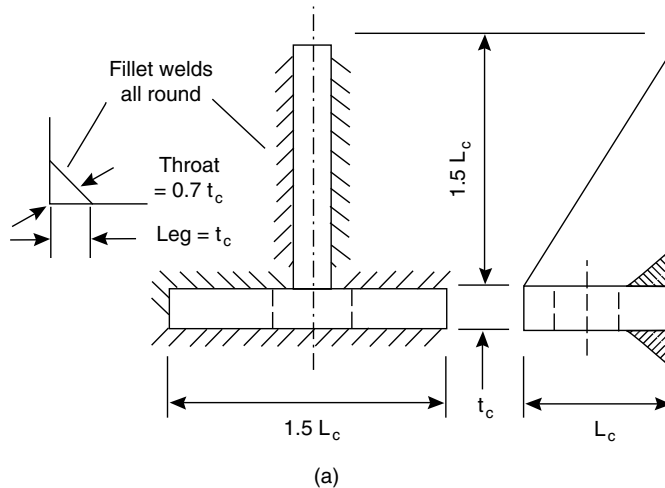


Figure 13.32. Bracket designs (a) Single gusset plate (b) Double gusset plate

Single-gusset plate design, Figure 13.32a:

$$F_{bs} = 60L_c t_c \quad (13.96)$$

Double-gusset plate design, Figure 13.32*b*:

$$F_{bs} = 120L_c t_c \quad (13.97)$$

where  $F_{bs}$  = maximum design load per bracket, N,  
 $L_c$  = the characteristic dimension of bracket (depth), mm,  
 $t_c$  = thickness of plate, mm.

## 13.10. BOLTED FLANGED JOINTS

Flanged joints are used for connecting pipes and instruments to vessels, for manhole covers, and for removable vessel heads when ease of access is required. Flanges may also be used on the vessel body, when it is necessary to divide the vessel into sections for transport or maintenance. Flanged joints are also used to connect pipes to other equipment, such as pumps and valves. Screwed joints are often used for small-diameter pipe connections, below 40 mm. Flanged joints are also used for connecting pipe sections where ease of assembly and dismantling is required for maintenance, but pipework will normally be welded to reduce costs.

Flanges range in size from a few millimetres diameter for small pipes, to several metres diameter for those used as body or head flanges on vessels.

### 13.10.1. Types of flange, and selection

Several different types of flange are used for various applications. The principal types used in the process industries are:

1. Welding-neck flanges.
2. Slip-on flanges, hub and plate types.
3. Lap-joint flanges.
4. Screwed flanges.
5. Blank, or blind, flanges.

*Welding-neck flanges*, Figure 13.33*a*: have a long tapered hub between the flange ring and the welded joint. This gradual transition of the section reduces the discontinuity stresses between the flange and branch, and increases the strength of the flange assembly. Welding-neck flanges are suitable for extreme service conditions; where the flange is likely to be subjected to temperature, shear and vibration loads. They will normally be specified for the connections and nozzles on process vessels and process equipment.

*Slip-on flanges*, Figure 13.33*b*: slip over the pipe or nozzle and are welded externally, and usually also internally. The end of the pipe is set back from 0 to 2.0 mm. The strength of a slip-on flange is from one-third to two-thirds that of the corresponding standard welding-neck flange. Slip-on flanges are cheaper than welding-neck flanges and are easier to align, but have poor resistance to shock and vibration loads. Slip-on flanges are generally used for pipe work. Figure 13.33*b* shows a forged flange with a hub; for light duties slip-on flanges can be cut from plate.

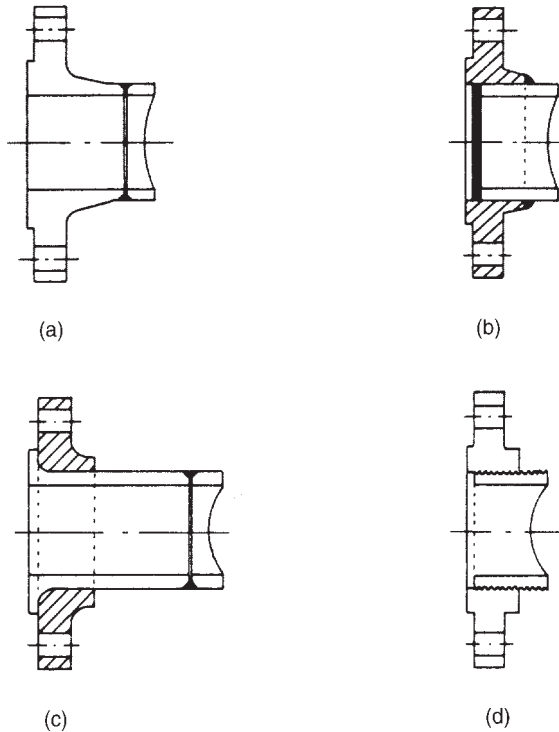


Figure 13.33. Flange types (a) Welding-neck (b) Slip-on (c) Lap-joint (d) Screwed

*Lap-joint flanges*, Figure 13.33c: are used for piped work. They are economical when used with expensive alloy pipe, such as stainless steel, as the flange can be made from inexpensive carbon steel. Usually a short lapped nozzle is welded to the pipe, but with some schedules of pipe the lap can be formed on the pipe itself, and this will give a cheap method of pipe assembly.

Lap-joint flanges are sometimes known as “Van-stone flanges”.

*Screwed flanges*, Figure 13.33d: are used to connect screwed fittings to flanges. They are also sometimes used for alloy pipe which is difficult to weld satisfactorily.

*Blind flanges* (blank flanges): are flat plates, used to blank off flange connections, and as covers for manholes and inspection ports.

### 13.10.2. Gaskets

Gaskets are used to make a leak-tight joint between two surfaces. It is impractical to machine flanges to the degree of surface finish that would be required to make a satisfactory seal under pressure without a gasket. Gaskets are made from “semi-plastic” materials; which will deform and flow under load to fill the surface irregularities between the flange faces, yet retain sufficient elasticity to take up the changes in the flange alignment that occur under load.

Table 13.4. Gasket materials  
(Based on a similar table in BS 5500: 1991; see BS PD 5500–2003)






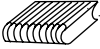









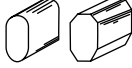
Gasket material	Gasket factor $m$	Min. design seating stress $y(N/mm^2)$	Sketches	Minimum gasket width (mm)
Rubber without fabric or a high percentage of asbestos fibre; hardness: below 75° IRH	0.50	0		10
75° IRH or higher	1.00	1.4		
Asbestos with a suitable binder for the operating conditions	3.2 mm thick	2.00		10
	1.6 mm thick	2.75		
	0.8 mm thick	3.50		
Rubber with cotton fabric insertion	1.25	2.8		10
Rubber with asbestos fabric insertion, with or without wire reinforcement	3-ply	2.25		10
	2-ply	2.50		
	1-ply	2.75		
Vegetable fibre	1.75	7.6		10
Spiral-wound metal, asbestos filled	Carbon	2.50		10
	Stainless or monel	3.00		
Corrugated metal, asbestos inserted or	Soft aluminium	2.50		10
	Soft copper or brass	2.75		
	Iron or soft steel	3.00		
Corrugated metal, jacketed asbestos filled	Monel or 4 to 6 per cent chrome	3.25		10
	Stainless steels	3.50		
	Soft aluminium	2.75		
Corrugated metal	Soft copper or brass	3.00		10
	Iron or soft steel	3.25		
	Monel or 4 to 6 per cent chrome	3.50		
Flat metal jacketed asbestos filled	Stainless steels	3.75		10
	Soft aluminium	3.25		
	Soft copper or brass	3.50		
Flat metal jacketed asbestos filled	Iron or soft steel	3.75		10
	Monel	3.50		
	4 to 6 per cent chrome	3.75		
Grooved metal	Stainless steels	3.75		10
	Soft aluminium	3.25		
	Soft copper or brass	3.50		
Grooved metal	Iron or soft steel	3.75		10
	Monel or 4 to 6 per cent chrome	3.75		
	Stainless steels	4.25		
Grooved metal	Soft aluminium	4.00		10
	Soft copper or brass	4.75		

Table 13.4. (continued)

Gasket material		Gasket factor $m$	Min. design seating stress $\gamma$ (N/mm <sup>2</sup> )	Sketches	Minimum gasket width (mm)
Solid flat metal	Iron or soft steel	5.50	124		6
	Monel or 4 to 6 per cent chrome	6.00	150		
	Stainless steels	6.50	179		
Ring joint	Iron or soft steel	5.50	124		6
	Monel or 4 to 6 per cent chrome	6.00	150		
	Stainless steels	6.50	179		

A great variety of proprietary gasket materials is used, and reference should be made to the manufacturers' catalogues and technical manuals when selecting gaskets for a particular application. Design data for some of the more commonly used gasket materials are given in Table 13.4. Further data can be found in the pressure vessel codes and standards and in various handbooks; Perry *et al.* (1997). The minimum seating stress  $\gamma$  is the force per unit area (pressure) on the gasket that is required to cause the material to flow and fill the surface irregularities in the gasket face.

The gasket factor  $m$  is the ratio of the gasket stress (pressure) under the operating conditions to the internal pressure in the vessel or pipe. The internal pressure will force the flanges' faces apart, so the pressure on the gasket under operating conditions will be lower than the initial tightening-up pressure. The gasket factor gives the minimum pressure that must be maintained on the gasket to ensure a satisfactory seal.

The following factors must be considered when selecting a gasket material:

1. The process conditions: pressure, temperature, corrosive nature of the process fluid.
2. Whether repeated assembly and disassembly of the joint is required.
3. The type of flange and flange face (see Section 13.10.3).

Up to pressures of 20 bar, the operating temperature and corrosiveness of the process fluid will be the controlling factor in gasket selection. Vegetable fibre and synthetic rubber gaskets can be used at temperatures of up to 100°C. Solid polyfluorocarbon (Teflon) and compressed asbestos gaskets can be used to a maximum temperature of about 260°C. Metal-reinforced gaskets can be used up to around 450°C. Plain soft metal gaskets are normally used for higher temperatures.

### 13.10.3. Flange faces

Flanges are also classified according to the type of flange face used. There are two basic types:

1. Full-faced flanges, Figure 13.34a: where the face contact area extends outside the circle of bolts; over the full face of the flange.

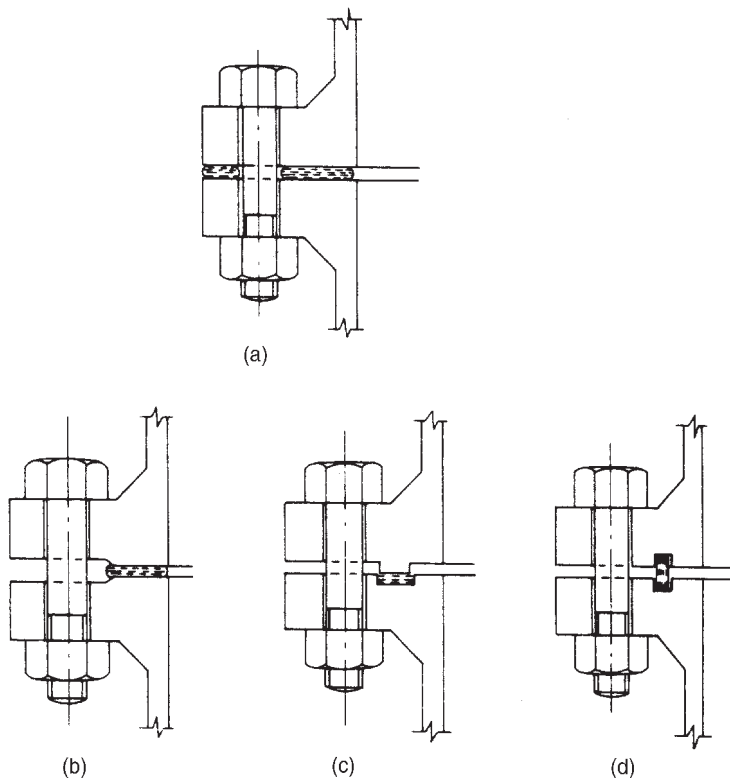


Figure 13.34. Flange types and faces (a) Full-face (b) Gasket within bolt circle (c) Spigot and socket (d) Ring type joint

2. Narrow-faced flanges, Figure 13.34*b, c, d*: where the face contact area is located within the circle of bolts.

Full face, wide-faced, flanges are simple and inexpensive, but are only suitable for low pressures. The gasket area is large, and an excessively high bolt tension would be needed to achieve sufficient gasket pressure to maintain a good seal at high operating pressures.

The raised face, narrow-faced, flange shown in Figure 13.34*b* is probably the most commonly used type of flange for process equipment.

Where the flange has a plain face, as in Figure 13.34*b*, the gasket is held in place by friction between the gasket and flange surface. In the spigot and socket, and tongue and grooved faces, Figure 13.34*c*, the gasket is confined in a groove, which prevents failure by “blow-out”. Matched pairs of flanges are required, which increases the cost, but this type is suitable for high pressure and high vacuum service. Ring joint flanges, Figure 13.34*d*, are used for high temperatures and high pressure services.

#### 13.10.4. Flange design

Standard flanges will be specified for most applications (see Section 13.10.5). Special designs would be used only if no suitable standard flange were available; or for large

flanges, such as the body flanges of vessels, where it may be cheaper to size a flange specifically for the duty required rather than to accept the nearest standard flange, which of necessity would be over-sized.

Figure 13.35 shows the forces acting on a flanged joint. The bolts hold the faces together, resisting the forces due to the internal pressure and the gasket sealing pressure. As these forces are offset the flange is subjected to a bending moment. It can be considered as a cantilever beam with a concentrated load. A flange assembly must be sized so as to have sufficient strength and rigidity to resist this bending moment. A flange that lacks sufficient rigidity will rotate slightly, and the joint will leak; Figure 13.36. The principles of flange design are discussed by Singh and Soler (1992), and Azbel and Cheremisinoff (1982). Singh and Soler give a computer programme for flange design.

Design procedures and work sheets for non-standard flanges are given in the national codes and standards.

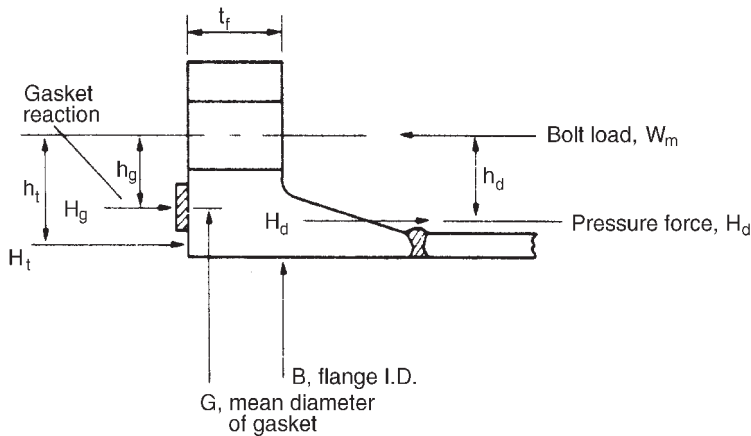


Figure 13.35. Forces acting on an integral flange

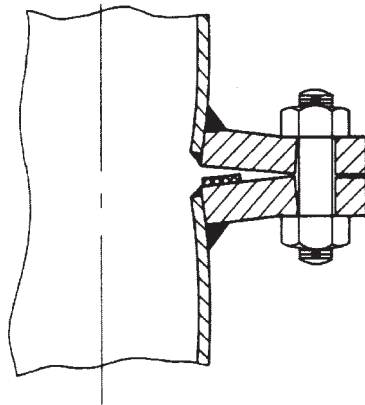


Figure 13.36. Deflection of a weak flange (exaggerated)



For design purposes, flanges are classified as integral or loose flanges.

Integral flanges are those in which the construction is such that the flange obtains support from its hub and the connecting nozzle (or pipe). The flange assembly and nozzle neck form an "integral" structure. A welding-neck flange would be classified as an integral flange.

Loose flanges are attached to the nozzle (or pipe) in such a way that they obtain no significant support from the nozzle neck and cannot be classified as an integral attachment. Screwed and lap-joint flanges are typical examples of loose flanges.

The design procedures given in the codes and standards can be illustrated by considering the forces and moments which act on an integral flange, Figure 13.35.

The total moment  $M_{op}$  acting on the flange is given by:

$$M_{op} = H_d h_d + H_t h_t + H_g h_g \quad (13.98)$$

Where  $H_g$  = gasket reaction (pressure force),  $= \pi G(2b)mP_i$

$H_t$  = pressure force on the flange face  $= H - H_d$ ,

$H$  = total pressure force  $= (\pi/4)G^2 P_i$ ,

$H_d$  = pressure force on the area inside the flange  $= (\pi/4)B^2 P_i$ ,

$G$  = mean diameter of the gasket,

$B$  = inside diameter of the flange,

$2b$  = effective gasket pressure width,

$b$  = effective gasket sealing width,

$h_d$ ,  $h_g$  and  $h_t$  are defined in Figure 13.35.

The minimum required bolt load under the operating conditions is given by:

$$W_{m1} = H + H_g \quad (13.99)$$

The forces and moments on the flange must also be checked under the bolting-up conditions.

The moment  $M_{atm}$  is given by:

$$M_{atm} = W_{m2} h_g \quad (13.100)$$

where  $W_{m2}$  is the bolt load required to seat the gasket, given by:

$$W_{m2} = y\pi Gb \quad (13.101)$$

where  $y$  is the gasket seating pressure (stress).

The flange stresses are given by:

$$\text{longitudinal hub stress,} \quad \sigma_{hb} = F_1 M \quad (13.102)$$

$$\text{radial flange stress,} \quad \sigma_{rd} = F_2 M \quad (13.103)$$

$$\text{tangential flange stress,} \quad \sigma_{tg} = F_3 M - F_4 \sigma_{rd} \quad (13.104)$$

where  $M$  is taken as  $M_{op}$  or  $M_{atm}$ , whichever is the greater; and the factors  $F_1$  to  $F_4$  are functions of the flange type and dimensions, and are obtained from equations and graphs given in the codes and standards (BS 5500, clause 3.8).

The flange must be sized so that the stresses given by equations 13.102 to 13.104 satisfy the following criteria:

$$\sigma_{hb} \not\leq 1.5f_{f0} \quad (13.105)$$

$$\sigma_{rd} \not\leq f_{f0} \quad (13.106)$$

$$\frac{1}{2}(\sigma_{hb} + \sigma_{rd}) \not\leq f_{f0} \quad (13.107)$$

$$\frac{1}{2}(\sigma_{hb} + \sigma_{tg}) \not\leq f_{f0} \quad (13.108)$$

where  $f_{f0}$  is the maximum allowable design stress for the flange material at the operating conditions.

The minimum bolt area required  $A_{bf}$  will be given by:

$$A_{bf} = \frac{W_m}{f_b} \quad (13.109)$$

where  $W_m$  is the greater value of  $W_{m1}$  or  $W_{m2}$ , and  $f_b$  the maximum allowable bolt stress. Standard size bolts should be chosen, sufficient to give the required area. The bolt size will not normally be less than 12 mm, as smaller sizes can be sheared off by over-tightening.

The bolt spacing must be selected to give a uniform compression of the gasket. It will not normally be less than 2.5 times the bolt diameter, to give sufficient clearance for tightening with a wrench or spanner. The following formula can be used to determine the maximum bolt spacing:

$$p_b = 2d_b + \frac{6t_f}{(m + 0.5)} \quad (13.110)$$

where  $p_b$  = bolt pitch (spacing), mm,

$d_b$  = bolt diameter, mm,

$t_f$  = flange thickness, mm,

$m$  = gasket factor.

### 13.10.5. Standard flanges

Standard flanges are available in a range of types, sizes and materials; and are used extensively for pipes, nozzles and other attachments to pressure vessels.

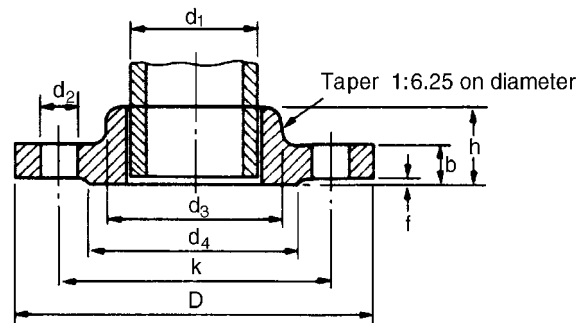
The proportions of standard flanges are set out in various codes and standards. A typical example of a standard flange design is shown in Figure 13.37. This was taken from BS 4504, which has now been superseded by the European standard BS EN 1092. The design of standard flanges is also specified in BS 1560.

In the United States, flanges are covered by the standards issued by the American National Standards Institute (ANSI). An abstract of the American standards is given by Perry *et al.* (1997).

Standard flanges are designated by class numbers, or rating numbers, which correspond to the primary service (pressure) rating of the flange at room temperature.

## STEEL SLIP-ON BOSS FLANGE FOR WELDING

Nominal pressure 6 bar



Nom. size	Pipe o.d. $d_1 \approx$	Flange			Raised face		Bolting	Drilling			Boss
		$D$	$b$	$h$	$d_4$	$f$		No.	$d_2$	$k$	
10	17.2	75	12	20	35	2	M10	4	11	50	25
15	21.3	80	12	20	40	2	M10	4	11	55	30
20	26.9	90	14	24	50	2	M10	4	11	65	40
25	33.7	100	14	24	60	2	M10	4	11	75	50
32	42.4	120	14	26	70	2	M12	4	14	90	60
40	48.3	130	14	26	80	3	M12	4	14	100	70
50	60.3	140	14	28	90	3	M12	4	14	110	80
65	76.1	160	14	32	110	3	M12	4	14	130	100
80	88.9	190	16	34	128	3	M16	4	18	150	110
100	114.3	210	16	40	148	3	M16	4	18	170	130
125	139.7	240	18	44	178	3	M16	8	18	200	160
150	168.3	265	18	44	202	3	M16	8	18	225	185
200	219.1	320	20	44	258	3	M16	8	18	280	240
250	273	375	22	44	312	3	M16	12	18	335	295
300	323.9	440	22	44	365	4	M20	12	22	395	355

Figure 13.37. Typical standard flange design (All dimensions mm)

The flange class number required for a particular application will depend on the design pressure and temperature, and the material of construction. The reduction in strength at elevated temperatures is allowed for by selecting a flange with a higher rating than the design pressure. For example, for a design pressure of 10 bar (150 psi) a BS 1560 carbon steel flange class 150 flange would be selected for a service temperature below 300°C; whereas for a service temperature of, say, 300°C a 300 pound flange would be specified. A typical pressure–temperature relationship for carbon steel flanges is shown in Table 13.5. Pressure–temperature ratings for a full range of materials can be obtained from the standards.

Typical designs, dimensioned, for welding-neck flanges over a range of pressure ratings are given in Appendix E. These can be used for preliminary designs. The current standards and suppliers' catalogues should be consulted before firming up the design.

Table 13.5. Typical pressure-temperature ratings for carbon steel flanges, BS 4504.

Nominal pressure (bar)	Design pressure at temperature, °C (bar)						
	up to 120	150	200	250	300	350	400
2.5	2.5	2.3	2.0	1.8	1.5	1.3	0.9
6	6.0	5.4	4.8	4.2	3.6	3.0	2.1
10	10	9.0	8.0	7.0	6.0	5.0	3.5
16	16	14.4	12.8	11.2	9.6	8.0	5.6
25	25	2.5	20.0	17.5	15.0	12.5	8.8
40	40	36.0	32.0	28.0	24.0	20.0	14.0

### 13.11. HEAT-EXCHANGER TUBE-PLATES

The tube-plates (tube-sheets) in shell and tube heat exchangers support the tubes, and separate the shell and tube side fluids (see Chapter 12). One side is subject to the shell-side pressure and the other the tube-side pressure. The plates must be designed to support the maximum differential pressure that is likely to occur. Radial and tangential bending stresses will be induced in the plate by the pressure load and, for fixed-head exchangers, by the load due to the differential expansion of the shell and tubes.

A tube-plate is essentially a perforated plate with an unperforated rim, supported at its periphery. The tube holes weaken the plate and reduce its flexural rigidity. The equations developed for the stress analysis of unperforated plates (Section 13.3.5) can be used for perforated plates by substituting “virtual” (effective) values for the elastic constants  $E$  and  $\nu$ , in place of the normal values for the plate material. The virtual elastic constants  $E'$  and  $\nu'$  are functions of the plate ligament efficiency, Figure 13.38; see O'Donnell and Langer (1962). The ligament efficiency of a perforated plate is defined as:

$$\lambda = \frac{p_h - d_h}{p_h} \quad (13.111)$$

where  $p_h$  = hole pitch,  
 $d_h$  = hole diameter.

The “ligament” is the material between the holes (that which holds the holes together). In a tube-plate the presence of the tubes strengthens the plate, and this is taken into account when calculating the ligament efficiency by using the inside diameter of the tubes in place of the hole diameter in equation 13.111.

Design procedures for tube-plates are given in BS PD 5500, and in the TEMA heat exchanger standards (see Chapter 12). The tube-plate must be thick enough to resist the bending and shear stresses caused by the pressure load and any differential expansion of the shell and tubes. The minimum plate thickness to resist bending can be estimated using an equation of similar form to that for plate end closures (Section 13.5.3).

$$t_p = C_{ph} D_p \sqrt{\frac{\Delta P'}{\lambda f_p}} \quad (13.112)$$

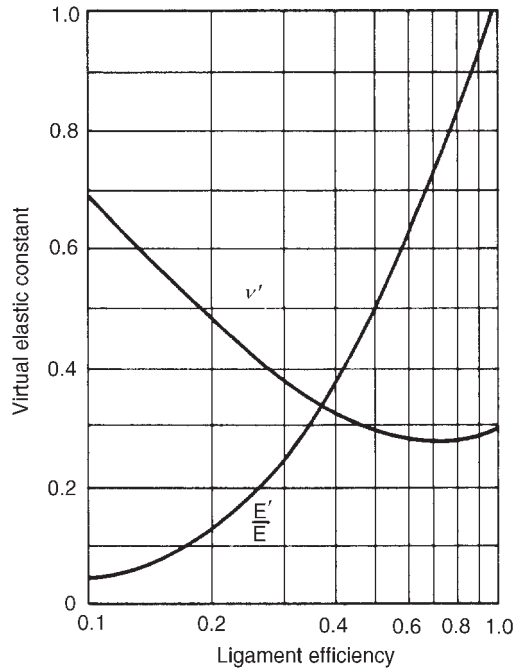


Figure 13.38. Virtual elastic constants

- where  $t_p$  = the minimum plate thickness,  
 $\Delta P'$  = the effective tube plate design pressure,  
 $\lambda$  = ligament efficiency,  
 $f_p$  = maximum allowable design stress for the plate,  
 $C_{ph}$  = a design factor,  
 $D_p$  = plate diameter.

The value of the design factor  $C_{ph}$  will depend on the type of head, the edge support (clamped or simply supported), the plate dimensions, and the elastic constants for the plate and tube material.

The tube-sheet design pressure  $\Delta P'$  depends on the type of exchanger. For an exchanger with confined heads or U-tubes it is taken as the maximum difference between the shell-side and tube-side operating pressures; with due consideration being given to the possible loss of pressure on either side. For exchangers with unconfined heads (plates fixed to the shell) the load on the tube-sheets due to differential expansion of the shell and tubes must be added to that due to the differential pressure.

The shear stress in the tube-plate can be calculated by equating the pressure force on the plate to the shear force in the material at the plate periphery. The minimum plate thickness to resist shear is given by:

$$t_p = \frac{0.155D_p \Delta P'}{\lambda \tau_p} \quad (13.113)$$

where  $\tau_p$  = the maximum allowable shear stress, taken as half the maximum allowable design stress for the material (see Section 13.3.2).

The design plate thickness is taken as the greater of the values obtained from equations 13.112 and 13.113 and must be greater than the minimum thickness given below:

Tube o.d. (mm)	Minimum plate thickness (mm)
25	$0.75 \times \text{tube o.d.}$
25–30	22
30–40	25
40–50	30

For exchangers with fixed tube-plates the longitudinal stresses in the tubes and shell must be checked to ensure that the maximum allowable design stresses for the materials are not exceeded. Methods for calculating these stresses are given in the standards.

A detailed account of the methods used for the stresses analysis of tube sheets is given by Jawad and Farr (1989), and Singh and Soler (1992). Singh and Soler give computer programs for the design of the principal types of tube-plate.

## 13.12. WELDED JOINT DESIGN

Process vessels are built up from preformed parts: cylinders, heads, and fittings, joined by fusion welding. Riveted construction was used extensively in the past (prior to the 1940s) but is now rarely seen.

Cylindrical sections are usually made up from plate sections rolled to the required curvature. The sections (strakes) are made as large as is practicable to reduce the number of welds required. The longitudinal welded seams are offset to avoid a conjunction of welds at the corners of the plates.

Many different forms of welded joint are needed in the construction of a pressure vessel. Some typical forms are shown in Figures 13.39 to 13.41.

The design of a welded joint should satisfy the following basic requirements:

1. Give good accessibility for welding and inspection.
2. Require the minimum amount of weld metal.
3. Give good penetration of the weld metal; from both sides of the joint, if practicable.
4. Incorporate sufficient flexibility to avoid cracking due to differential thermal expansion.

The preferred types of joint, and recommended designs and profiles, are given in the codes and standards.

The correct form to use for a given joint will depend on the material, the method of welding (machine or hand), the plate thickness, and the service conditions. Double-sided V- or U-sections are used for thick plates, and single V- or U-profiles for thin plates. A backing strip is used where it is not possible to weld from both sides. Lap joints are seldom used for pressure vessels construction, but are used for atmospheric pressure storage tanks.

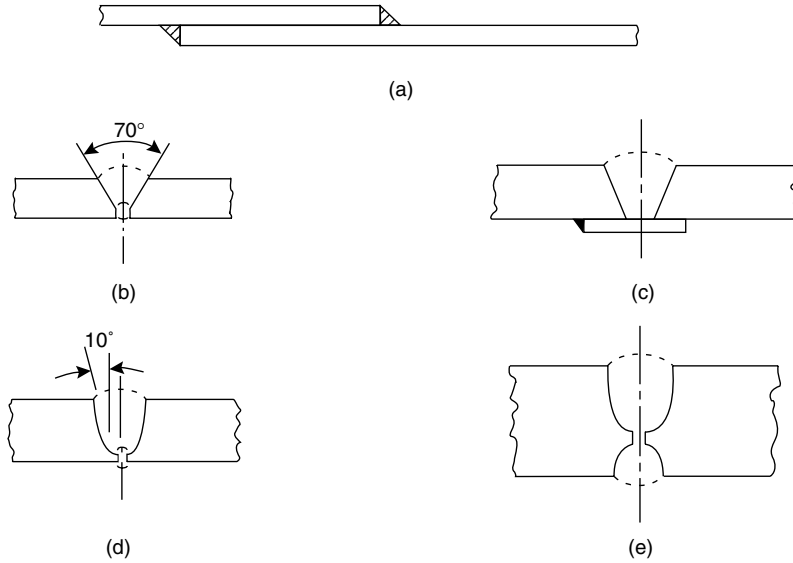


Figure 13.39. Weld profiles; (b to e) butt welds (a) Lap joint (b) Single 'V' (c) Backing strip (d) Single 'U' (e) Double 'U'

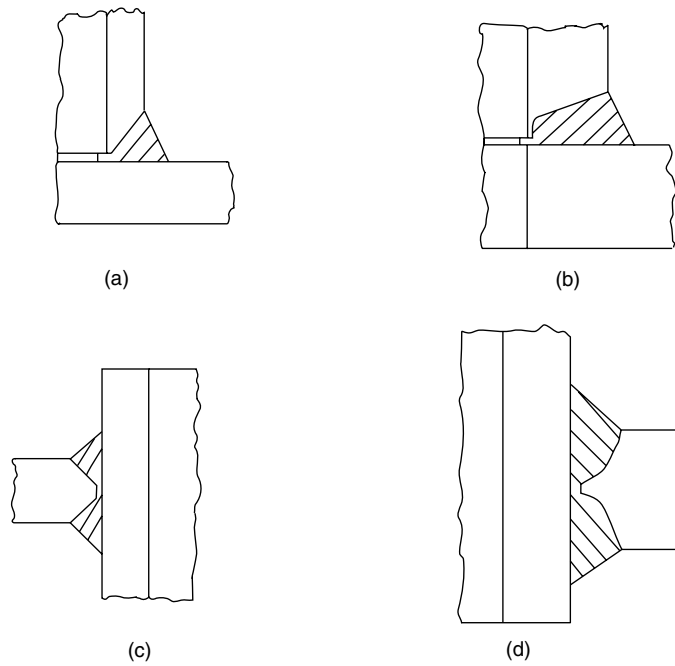


Figure 13.40. Typical weld profiles—Branches (a), (b) Set-on branches (c), (d) Set-in branches

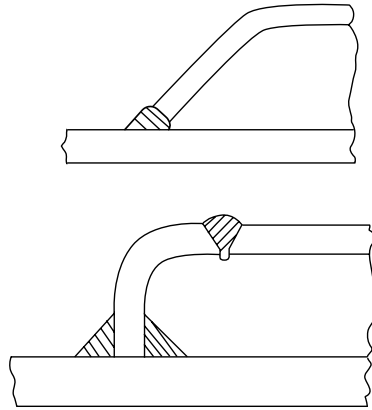


Figure 13.41. Typical construction methods for welded jackets

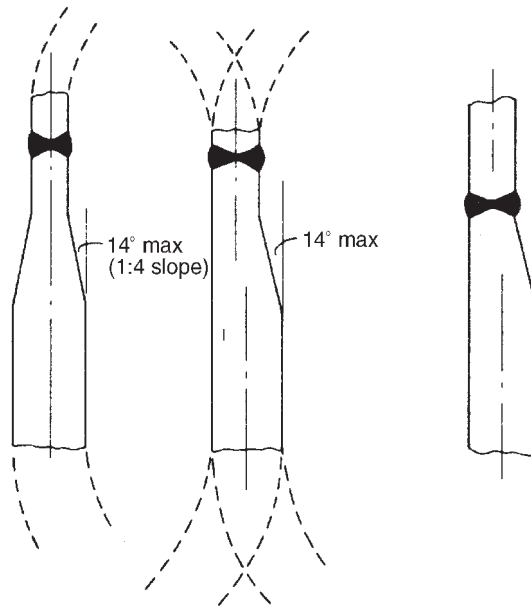


Figure 13.42. Transition between plates of unequal thickness

Where butt joints are made between plates of different thickness, the thicker plate is reduced in thickness with a slope of not greater than 1 in 4 ( $14^\circ$ ) (Figure 13.42).

The local heating, and consequent expansion, that occurs during welding can leave the joint in a state of stress. These stresses are relieved by post-welding heat treatment. Not all vessels will be stress relieved. Guidance on the need for post-welding heat treatment is given in the codes and standards, and will depend on the service and conditions, materials of construction, and plate thickness.



To ensure that a satisfactory quality of welding is maintained, welding-machine operators and welders working on the pressure parts of vessels are required to pass welder approval tests; which are designed to test their competence to make sound welds.

### 13.13. FATIGUE ASSESSMENT OF VESSELS

During operation the shell, or components of the vessel, may be subjected to cyclic stresses. Stress cycling can arise from the following causes:

1. Periodic fluctuations in operating pressure.
2. Temperature cycling.
3. Vibration.
4. "Water hammer".
5. Periodic fluctuation of external loads.

A detailed fatigue analysis is required if any of these conditions is likely to occur to any significant extent. Fatigue failure will occur during the service life of the vessel if the endurance limit (number of cycles for failure) at the particular value of the cyclic stress is exceeded. The codes and standards should be consulted to determine when a detailed fatigue analysis must be undertaken.

### 13.14. PRESSURE TESTS

The national pressure vessel codes and standards require that all pressure vessels be subjected to a pressure test to prove the integrity of the finished vessel. A hydraulic test is normally carried out, but a pneumatic test can be substituted under circumstances where the use of a liquid for testing is not practical. Hydraulic tests are safer because only a small amount of energy is stored in the compressed liquid. A standard pressure test is used when the required thickness of the vessel parts can be calculated in accordance with the particular code or standard. The vessel is tested at a pressure above the design pressure, typically 25 to 30 per cent. The test pressure is adjusted to allow for the difference in strength of the vessel material at the test temperature compared with the design temperature, and for any corrosion allowance.

Formulae for determining the appropriate test pressure are given in the codes and standards; such as that given below:

$$\text{Test pressure} = 1.25 \left[ P_d \frac{f_a}{f_n} \times \frac{t}{(t - c)} \right] \quad (13.114)$$

where  $P_d$  = design pressure, N/mm<sup>2</sup>,

$f_a$  = nominal design strength (design stress) at the test temperature, N/mm<sup>2</sup>,

$f_n$  = nominal design strength at the design temperature, N/mm<sup>2</sup>,

$c$  = corrosion allowance, mm,

$t$  = actual plate thickness, mm.

When the required thickness of the vessel component parts cannot be determined by calculation in accordance with the methods given, the codes and standards require that a hydraulic proof test be carried out. In a proof test the stresses induced in the vessel

during the test are monitored using strain gauges, or similar techniques. The requirements for the proof testing of vessels are set out in the codes and standards.

### 13.15. HIGH-PRESSURE VESSELS

High pressures are required for many commercial chemical processes. For example, the synthesis of ammonia is carried out at reactor pressures of up to 1000 bar, and high-density polyethylene processes operate up to 1500 bar.

Only a brief discussion of the design of vessels for operation at high pressures will be given in this section; sufficient to show the fundamental limitations of single-wall (monobloc) vessels, and the construction techniques that are used to overcome this limitation. A full discussion of the design and construction of high-pressure vessels and ancillary equipment (pumps, compressors, valves and fittings) is given in the books by Fryer and Harvey (1997) and Jawad and Farr (1989); see also the relevant ASME code, ASME (2004).

#### 13.15.1. Fundamental equations

Thick walls are required to contain high pressures, and the assumptions made in the earlier sections of this chapter to develop the design equations for “thin-walled” vessels will not be valid. The radial stress will not be negligible and the tangential (hoop) stress will vary across the wall.

Consider the forces acting on the elemental section of the wall of the cylinder shown in Figure 13.43. The cylinder is under an internal pressure  $P_i$  and an external pressure  $P_e$ . The conditions for static equilibrium, with the forces resolved radially, give:

$$\sigma_r r \delta\phi - 2\sigma_t \delta r \sin \frac{\delta\phi}{2} - (\sigma_r + \delta\sigma_r)(r + \delta r)\delta\phi = 0$$

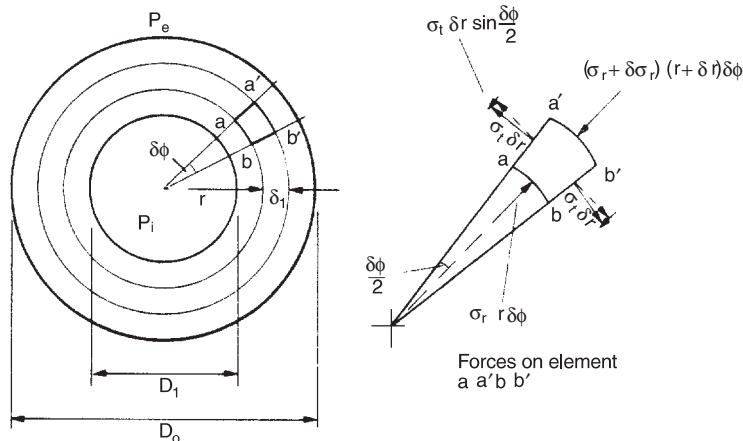


Figure 13.43. Thick cylinder

multiplying out taking the limit gives:

$$\sigma_t + r \frac{d\sigma_r}{dr} + \sigma_r = 0 \quad (13.115)$$

A second equation relating the radial and tangential stresses can be written if the longitudinal strain  $\varepsilon_L$  and stress  $\sigma_L$  are taken to be constant across the wall; that is, that there is no distortion of plane sections, which will be true for sections away from the ends. The longitudinal strain is given by:

$$\varepsilon_L = \frac{1}{E}[\sigma_L - (\sigma_t - \sigma_r)v] \quad (13.116)$$

If  $\varepsilon_L$  and  $\sigma_L$  are constant, then the term  $(\sigma_t - \sigma_r)$  must also be constant, and can be written as:

$$(\sigma_t - \sigma_r) = 2A \quad (13.117)$$

where  $A$  is an arbitrary constant.

Substituting for  $\sigma_t$  in equation 13.115 gives:

$$2\sigma_r + r \frac{d\sigma_r}{dr} = -2A$$

and integrating

$$\sigma_r = -A + \frac{B'}{r^2} \quad (13.118)$$

where  $B'$  is the constant of integration.

In terms of the cylinder diameter, the equations can be written as:

$$\sigma_r = -A + \frac{B}{d^2} \quad (13.119)$$

$$\sigma_t = A + \frac{B}{d^2} \quad (13.120)$$

These are the fundamental equations for the design of thick cylinders and are often referred to as Lamé's equations, as they were first derived by Lamé and Clapeyron (1833). The constants  $A$  and  $B$  are determined from the boundary conditions for the particular loading condition.

Most high-pressure process vessels will be under internal pressure only, the atmospheric pressure outside a vessel will be negligible compared with the internal pressure. The boundary conditions for this loading condition will be:

$$\sigma_r = P_i \text{ at } d = D_i$$

$$\sigma_r = 0 \text{ at } d = D_o$$

Substituting these values in equation 13.119 gives

$$P_i = -A + \frac{B}{D_i^2}$$

and 
$$0 = -A + \frac{B}{D_o^2}$$

subtracting gives

$$P_i = B \left[ \frac{1}{D_i^2} - \frac{1}{D_o^2} \right]$$

hence

$$B = P_i \frac{(D_i^2 D_o^2)}{(D_o^2 - D_i^2)}$$

and

$$A = P_i \frac{D_i^2}{(D_o^2 - D_i^2)}$$

Substituting in equations 13.119 and 13.120 gives:

$$\sigma_r = P_i \left[ \frac{D_i^2(D_o^2 - d^2)}{d^2(D_o^2 - D_i^2)} \right] \quad (13.121)$$

$$\sigma_t = P_i \left[ \frac{D_i^2(D_o^2 + d^2)}{d^2(D_o^2 - D_i^2)} \right] \quad (13.122)$$

The stress distribution across the vessel wall is shown plotted in Figure 13.44. The maximum values will occur at the inside surface, at  $d = D_i$ .

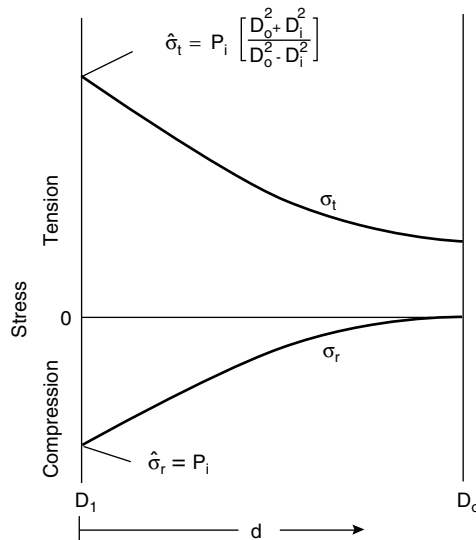


Figure 13.44. Stress distribution in wall of a monobloc cylinder

Putting  $K = D_o/D_i$ , the maximum values are given by:

$$\hat{\sigma}_r = P_i \text{ (compressive)} \quad (13.123)$$

$$\hat{\sigma}_t = P_i \left[ \frac{K^2 + 1}{K^2 - 1} \right] \quad (13.124)$$

An expression for the longitudinal stress can be obtained by equating forces in the axial direction:

$$\sigma_L \frac{\pi}{4} (D_o^2 - D_i^2) = P_i \frac{\pi D_i^2}{4}$$

hence

$$\sigma_L = \frac{P_i D_i^2}{(D_o^2 - D_i^2)} = \frac{P_i}{(K^2 - 1)} \quad (13.125)$$

The maximum shear stress will be given by (see Section 13.3.1):

$$\hat{\tau} = \frac{1}{2}(\hat{\sigma}_t + \hat{\sigma}_r) = \frac{P_i K^2}{(K^2 - 1)} \quad (13.126)$$

### **Theoretical maximum pressure**

If the maximum shear stress theory is taken as the criterion of failure (Section 13.3.2), then the maximum pressure that a monobloc vessel can be designed to withstand without failure is given by:

$$\hat{\tau} = \frac{\sigma'_e}{2} = \frac{P_i K^2}{(K^2 - 1)}$$

hence

$$\hat{P}_i = \frac{\sigma'_e}{2} \left[ \frac{K^2 - 1}{K^2} \right] \quad (13.127)$$

where  $\sigma'_e$  is the elastic limit stress for the material of construction divided by a suitable factor of safety. As the wall thickness is increased the term  $(K^2 - 1)/K^2$  tends to 1,

and

$$\hat{P}_i = \frac{\sigma'_e}{2} \quad (13.128)$$

which sets an upper limit on the pressure that can be contained in a monobloc cylinder.

Manning (1947) has shown that the maximum shear strain energy theory of failure (due to Mises (1913)) gives a closer fit to experimentally determined failure pressures for monobloc cylinders than the maximum shear stress theory. This criterion of failure gives:

$$\hat{P}_i = \frac{\sigma'_e}{\sqrt{3}} \quad (13.129)$$

From Figure (13.44) it can be seen that the stress falls off rapidly across the wall and that the material in the outer part of the wall is not being used effectively. The material can be used more efficiently by prestressing the wall. This will give a more uniform stress distribution under pressure. Several different “prestressing” techniques are used; the principal methods are described briefly in the following sections.

### 13.15.2. Compound vessels

#### ***Shrink-fitted cylinders***

Compound vessels are made by shrinking one cylinder over another. The inside diameter of the outer cylinder is made slightly smaller than the outer diameter of the inner cylinder, and is expanded by heating to fit over the inner. On cooling the outer cylinder contracts and places the inner under compression. The stress distribution in a two-cylinder compound vessel is shown in Figure 13.45; more than two cylinders may be used.

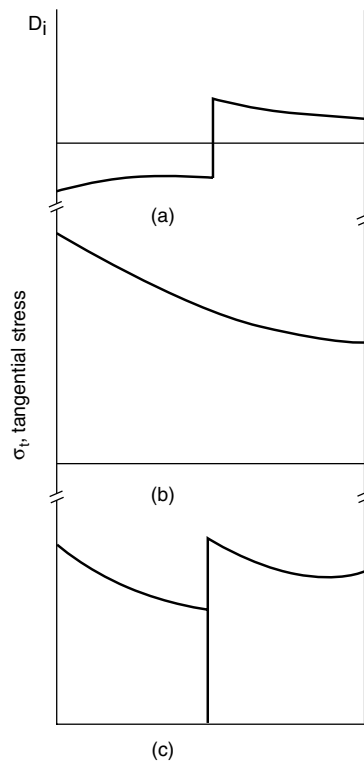


Figure 13.45. Stress distribution in a shrink-fitted compound cylinder (a) Due to shrinkage (b) Due to pressure (c) Combined (a + b)

Shrink-fitted compound cylinders are used for small-diameter vessels, such as compressor cylinder barrels. The design of shrink-fitted compound cylinders is discussed by Manning (1947) and Jawad and Farr (1989).

#### ***Multilayer vessels***

Multilayer vessels are made by wrapping several layers of relatively thin plate round a central tube. The plates are heated, tightened and welded, and this gives the desired stress distribution in the compound wall. The vessel is closed with forged heads. A typical

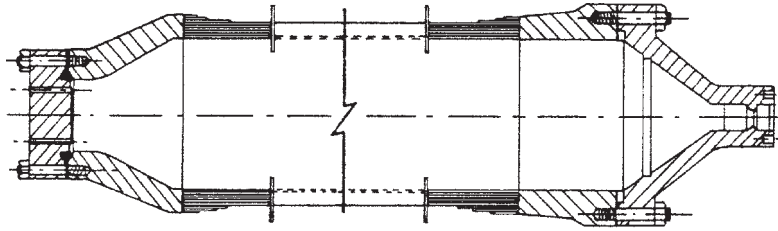


Figure 13.46. Multilayer construction

design is shown in Figure 13.46. This construction technique is discussed by Jasper and Scudder (1941) and Jawad and Farr (1989).

### ***Wound vessels***

Cylindrical vessels can be reinforced by winding on wire or thin ribbons. Winding on the wire under tension places the cylinder under compression. For high-pressure vessels special interlocking strips are used, such as those shown in Figure 13.47. The interlocking gives strength in the longitudinal direction and a more uniform stress distribution. The strips may be wound on hot to increase the prestressing. This type of construction is described by Birchall and Lake (1947). Wire winding was used extensively for the barrels of large guns.

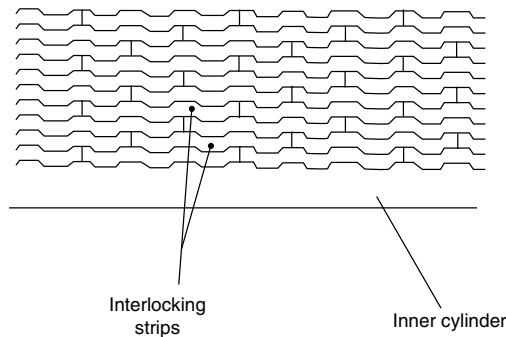


Figure 13.47. Strip wound vessel

### **13.15.3. Autofrettage**

Autofrettage is a technique used to prestress the inner part of the wall of a monobloc vessel, to give a similar stress distribution to that obtained in a shrink-fitted compound cylinder. The finished vessel is deliberately over pressurised by hydraulic pressure. During this process the inner part of the wall will be more highly stressed than the outer part and will undergo plastic strain. On release of the “autofrettage” pressure the inner part, which is now over-size, will be placed under compression by the elastic contraction of the outer part, which gives a residual stress distribution similar to that obtained in a two-layer shrink-fitted compound cylinder. After straining the vessel is annealed at a relatively low temperature, approximately 300°C. The straining also work-hardens the inner part of the

wall. The vessel can be used at pressures up to the “autofrettage” pressure without further permanent distortion.

The autofrettage technique is discussed by Manning (1950) and Jawad and Farr (1989).

### 13.16. LIQUID STORAGE TANKS

Vertical cylindrical tanks, with flat bases and conical roofs, are universally used for the bulk storage of liquids at atmospheric pressure. Tank sizes vary from a few hundred gallons (tens of cubic metres) to several thousand gallons (several hundred cubic metres).

The main load to be considered in the design of these tanks is the hydrostatic pressure of the liquid, but the tanks must also be designed to withstand wind loading and, for some locations, the weight of snow on the tank roof.

The minimum wall thickness required to resist the hydrostatic pressure can be calculated from the equations for the membrane stresses in thin cylinders (Section 13.3.4):

$$e_s = \frac{\rho_L H_L g}{2 f_t J} \frac{D_t}{10^3} \quad (13.130)$$

where  $e_s$  = tank thickness required at depth  $H_L$ , mm,

$H_L$  = liquid depth, m,

$\rho_L$  = liquid density, kg/m<sup>3</sup>,

$J$  = joint factor (if applicable),

$g$  = gravitational acceleration, 9.81 m/s<sup>2</sup>,

$f_t$  = design stress for tank material, N/mm<sup>2</sup>,

$D_t$  = tank diameter, m.

The liquid density should be taken as that of water (1000 kg/m<sup>3</sup>), unless the process liquid has a greater density.

For small tanks a constant wall thickness would normally be used, calculated at the maximum liquid depth.

With large tanks, it is economical to take account of the variation in hydrostatic pressure with depth, by increasing the plate thickness progressively from the top to bottom of the tank. Plate widths of 2 m (6 ft) are typically used in tank construction.

The roofs of large tanks need to be supported by a steel framework; supported on columns in very large-diameter tanks.

The design and construction of atmospheric storage tanks for the petroleum industry are covered by British Standard BS 2654, and the American Petroleum Industry standards API 650 (2003) and 620 (2002). The design of storage tanks is covered in the books by Myers (1997), and Jawad and Farr (1989). See also the papers by Debbam *et al.* (1968) and Zick and McGarth (1968).

### 13.17. MECHANICAL DESIGN OF CENTRIFUGES

#### 13.17.1. Centrifugal pressure

The fluid in a rotating centrifuge exerts pressure on the walls of the bowl or basket. The minimum wall thickness required to contain this pressure load can be determined in a



similar manner to that used for determining the wall thickness of a pressure vessel under internal pressure. If the bowl contains a single homogeneous liquid, Figure 13.48a, the fluid pressure is given by:

$$P_f = \frac{1}{2}\rho_L\omega^2(R_1^2 - R_2^2) \quad (13.131)$$

where  $P_f$  = centrifugal pressure, N/m<sup>2</sup>,  
 $\rho_L$  = liquid density, kg/m<sup>3</sup>,  
 $\omega$  = rotational speed of the centrifuge, radians/s,  
 $R_1$  = inside radius of the bowl, m,  
 $R_2$  = radius of the liquid surface, m.

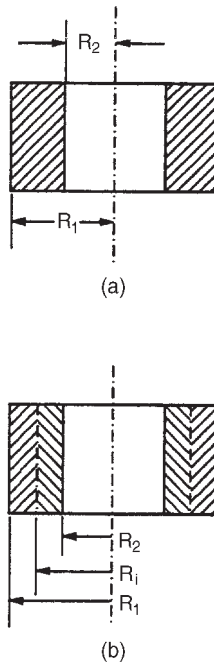


Figure 13.48. Centrifugal fluid pressure (a) Single fluid (b) Two fluids

For design, the maximum fluid pressure will occur when the bowl is full,  $R_2 = 0$ .

If the centrifuge is separating two immiscible liquids, Figure 13.48b, the pressure will be given by:

$$P_f = \frac{1}{2}\omega^2[\rho_{L1}(R_1^2 - R_i^2) + \rho_{L2}(R_i^2 - R_2^2)] \quad (13.132)$$

where  $\rho_{L1}$  = density of the heavier liquid, kg/m<sup>3</sup>,  
 $\rho_{L2}$  = density of the lighter liquid, kg/m<sup>3</sup>,  
 $R_i$  = radius of the interface between the two liquids, m.

If the machine is separating a solid-liquid mixture, the mean density of the slurry in the bowl should be used in equation 13.131.

The shell of an empty centrifuge bowl will be under stress due to the rotation of the bowl's own mass; this "self-pressure"  $P_m$  is given by:

$$P_m = \frac{1}{2}\omega^2\rho_m[(R_1 + t)^2 - R_1^2] \quad (13.133)$$

where  $\rho_m$  = density of the bowl material, kg/m<sup>3</sup>,  
 $t$  = bowl wall thickness, m.

The minimum wall thickness required can be estimated using the equations for membrane stress derived in Section 13.3.4. For a solid bowl

$$e_c = \frac{P_t R_1}{f_m \times 10^3} \quad (13.134)$$

where  $P_t$  = the total (maximum) pressure (fluid + self-pressure), N/m<sup>2</sup>,  
 $f_m$  = maximum allowable design stress for the bowl material, N/mm<sup>2</sup>,  
 $e_c$  = wall thickness, mm.

With a perforated basket the presence of the holes will weaken the wall. This can be allowed for by introducing a "ligament efficiency" into equation 13.134 (see Section 13.11)

$$e_c = \frac{P_t R_1}{f_m \times 10^3 \lambda} \quad (13.135)$$

where  $\lambda$  = ligament efficiency =  $(p_h - d_h)/(p_h)$ ,  
 $p_h$  = hole pitch,  
 $d_h$  = hole diameter.

Equations 13.134 and 13.135 can also be used to estimate the maximum safe load (or speed) for an existing centrifuge, if the service is to be changed.

In deriving these equations no account was taken of the strengthening effect of the bottom and top rings of the bowl or basket; so the equations will give estimates that are on the safe side. Strengthening hoops or bands are used on some basket designs.

### 13.17.2. Bowl and spindle motion: critical speed

Centrifuges are classified according to the form of mounting used: fixed or free spindle. With fixed-spindle machines, the bearings are rigidly mounted; whereas, in a free spindle, or self-balancing, machine a degree of "free-play" is allowed in the spindle mounting. The amount of movement of the spindle is restrained by some device, such as a rubber buffer. This arrangement allows the centrifuge to operate with a certain amount of out-of-balance loading without imposing an undue load on the bearings. Self-balancing centrifuges can be under or over-driven; that is, with the drive mounted below or above the bowl. Severe vibration can occur in the operation of fixed-spindle centrifuges and these are often suspended on rods, supported from columns mounted on an independent base, to prevent the vibration being transmitted to the building structure.

### Critical speed

If the centre of gravity of the rotating load does not coincide with the axis of rotation of the bowl an uneven force will be exerted on the machine spindle. In a self-balancing machine (or a suspended fixed-spindle machine) this will cause the spindle to deflect from the vertical position and the bowl will develop a whirling vibration. The phenomenon is analogous with the whirling of the shafts in other rotating machinery; such as compressors, pumps, and agitators; which is considered under the general heading of the “whirling of shafts” in standard texts on the “Theory of Machines”.

The simple analysis given below is based on that used to determine the whirling speed of a shaft with a single concentrated mass. Figure 13.49 shows the position of the centre of gravity of a rotating mass  $m_c$  with an initial displacement  $h_c$ . Let  $x_c$  be the additional displacement caused by the action of centrifugal force, and  $s$  the restoring force, assumed to be proportional to the displacement. The radial outward centrifugal force due to the displacement of the centre of the gravity from the axis of rotation will be  $= m_c \omega^2 (x_c + h_c)$ . This is balanced by the inward action of the restoring force  $= s x_c$ .

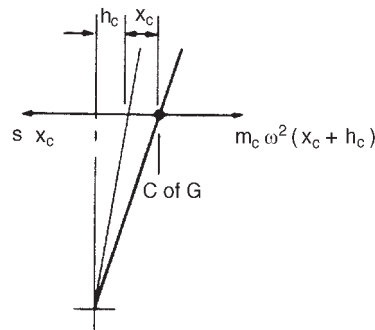


Figure 13.49. Displacement of centre of gravity of a centrifuge bowl

Equating the two forces:

$$m_c \omega^2 (x_c + h_c) = s x_c$$

from which

$$\frac{x_c}{h_c} = \frac{1}{\left(\frac{s}{m_c \omega^2}\right) - 1} \quad (13.136)$$

It can be seen by inspection of equation 13.136 that the deflection (the ratio  $x_c/h_c$ ) will become indefinitely large when the term  $s/m_c \omega^2 = 1$ ; the corresponding value of  $\omega$  is known as the critical, or whirling, speed. Above the critical speed the term  $s/m_c \omega^2$  becomes negative, and  $x_c/h_c$  tends to a limiting value of  $-1$  at high speeds. This shows that if the centrifuge is run at speeds in excess of the critical speed the tendency is for the spindle to deflect so that the axis of rotation passes through the centre of gravity of the system. The sequence of events as a self-balancing centrifuge run up to speed is shown

in Figure 13.50. In practice, a centrifuge is accelerated rapidly to get through the critical speed range quickly, and the observed deflections are not great.

It can be seen from equation 13.136 that the critical speed of a centrifuge will depend on the mass of the bowl and the magnitude of the restoring force; it will also depend on the dimensions of the machine and the length of the spindle. The critical speed of a simple system can be calculated, but for a complex system, such as loaded centrifuges, the critical speed must be determined by experiment. It can be shown that the critical speed of a rotating system corresponds with the natural frequency of vibration of the system.

A low critical speed is desired, as less time is then spent accelerating the bowl through the critical range. Suspended fixed-spindle centrifuges generally have a low critical speed.

### Precession

In addition to the whirling vibration due to an out-of-balance force, another type of motion can occur in a free-spindle machine. When the bowl or basket is tilted the spindle may move in a circle. This slow gyratory motion is known as “precession”, and is similar to the “precession” of a gyroscope. It is usually most pronounced at high speeds, above the critical speed.

A complete analysis of the motion of centrifuges is given by Alliott (1924, 1926).

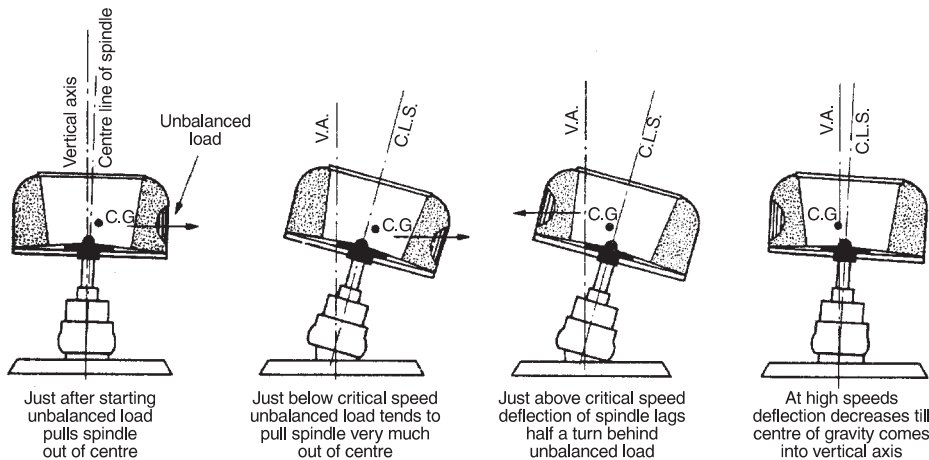


Figure 13.50. Diagram of action of self-balancing centrifuge, showing motion of centre of gravity and unbalanced load with increasing speed

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## Standards

### *American Petroleum Institute, Washington DC, USA*

- API 620 (2002) Design and construction of large, welded, low pressure storage tanks, 10th edn.
- API 650 (2002) Welded steel tanks for oil storage, 10th edn.

### *British Standards Institute, London, UK*

- BS 2654 (1989) Specification for the manufacture of welded non-refrigerated storage tanks for the petroleum industry.
- BS 4494 (1987) Specification for vessels and tanks in reinforced plastics.
- BS CP 5500 (2003) Specification for unfired fusion welded pressure vessels.
- BS EN 13445, Unfired pressure vessels

### *American Society of Mechanical Engineers, New York, USA*

- ASME Boiler and pressure vessel code (2204)

## 13.19. NOMENCLATURE

		Dimensions in <b>MLT</b>
$A$	Arbitrary constant in equation 13.117	$\text{ML}^{-1}\text{T}^{-2}$
$A_{bf}$	Total bolt area required for a flange	$\text{L}^2$
$A_1$	Area removed in forming hole	$\text{L}^2$
$A_2$	Area of compensation	$\text{L}^2$
$a$	Diameter of flat plate	$\text{L}$
$2a$	Major axis of ellipse	$\text{L}$
$a_e$	Acceleration due to an earthquake	$\text{LT}^{-2}$

<i>B</i>	Inside diameter of flange	<b>L</b>
<i>B</i>	Arbitrary constant in equation 13.120	<b>MLT<sup>-2</sup></b>
<i>B'</i>	Constant of integration in equation 13.118	<b>MLT<sup>-2</sup></b>
<i>b</i>	Effective sealing width of gasket	<b>L</b>
<i>2b</i>	Minor axis of ellipse	<b>L</b>
<i>C</i>	Constant in equation 13.34	—
<i>C<sub>c</sub></i>	Design factor in equation 13.46	—
<i>C<sub>d</sub></i>	Drag coefficient in equation 13.79	—
<i>C<sub>e</sub></i>	Seismic constant	—
<i>C<sub>h</sub></i>	Constant in equation 13.85	—
<i>C<sub>p</sub></i>	Constant in equation 13.34	—
<i>C<sub>ph</sub></i>	Design factor in equation 13.112	—
<i>C<sub>s</sub></i>	Design factor in equation 13.44	—
<i>c</i>	Corrosion allowance	<b>L</b>
<i>D</i>	Diameter	<b>L</b>
<b>D</b>	Flexural rigidity	<b>ML<sup>2</sup>T<sup>-2</sup></b>
<i>D<sub>b</sub></i>	Bolt circle diameter	<b>L</b>
<i>D<sub>c</sub></i>	Diameter of cone at point of interest	<b>L</b>
<i>D<sub>e</sub></i>	Nominal diameter of flat end	<b>L</b>
<i>D<sub>eff</sub></i>	Effective diameter of column for wind loading	<b>L</b>
<i>D<sub>i</sub></i>	Internal diameter	<b>L</b>
<i>D<sub>m</sub></i>	Mean diameter	<b>L</b>
<i>D<sub>o</sub></i>	Outside diameter	<b>L</b>
<i>D<sub>p</sub></i>	Plate diameter, tube-sheet	<b>L</b>
<i>D<sub>r</sub></i>	Diameter of stiffening ring	<b>L</b>
<i>D<sub>s</sub></i>	Skirt internal diameter	<b>L</b>
<i>D<sub>t</sub></i>	Tank diameter	<b>L</b>
<i>d</i>	Diameter at point of interest, thick cylinder	<b>L</b>
<i>d<sub>b</sub></i>	Bolt diameter	<b>L</b>
<i>d<sub>h</sub></i>	Hole diameter	<b>L</b>
<i>d<sub>r</sub></i>	Diameter of reinforcement pad	<b>L</b>
<i>E</i>	Young's modulus	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>e</i>	Minimum plate thickness	<b>L</b>
<i>e<sub>c</sub></i>	Minimum thickness of conical section	<b>L</b>
<i>e<sub>k</sub></i>	Minimum thickness of conical transition section	<b>L</b>
<i>e<sub>m</sub></i>	Minimum wall thickness, centrifuge	<b>L</b>
<i>e<sub>s</sub></i>	Minimum thickness of tank	<b>L</b>
<i>F<sub>b</sub></i>	Compressive load on base ring, per unit length	<b>MT<sup>-2</sup></b>
<i>F<sub>bs</sub></i>	Load supported by bracket	<b>MLT<sup>-2</sup></b>
<i>F<sub>c</sub></i>	Critical buckling load for a ring, per unit length	<b>MT<sup>-2</sup></b>
<i>F<sub>p</sub></i>	Local, concentrated, wind load	<b>MLT<sup>-2</sup></b>
<i>F<sub>r</sub></i>	Load on stiffening ring, per unit length	<b>MT<sup>-2</sup></b>
<i>F<sub>s</sub></i>	Shear force due an earthquake	<b>MLT<sup>-2</sup></b>
<i>F<sub>w</sub></i>	Loading due to wind pressure, per unit length	<b>MT<sup>-2</sup></b>
<i>F<sub>1</sub></i>	Factor in equation 13.102	<b>L<sup>-3</sup></b>
<i>F<sub>2</sub></i>	Factor in equation 13.103	<b>L<sup>-3</sup></b>
<i>F<sub>3</sub></i>	Factor in equation 13.104	<b>L<sup>-3</sup></b>
<i>F<sub>4</sub></i>	Factor in equation 13.104	—
<i>f</i>	Maximum allowable stress (design stress)	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>a</sub></i>	Nominal design strength at test temperature	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>b</sub></i>	Maximum allowable bolt stress	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>c</sub></i>	Maximum allowable bearing pressure	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f'<sub>c</sub></i>	Actual bearing pressure	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>f</sub></i>	Maximum allowable design stress for flange material	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>m</sub></i>	Maximum allowable stress for centrifuge material	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>n</sub></i>	Nominal design strength at design temperature	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>p</sub></i>	Maximum allowable design stress for plate	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>r</sub></i>	Maximum allowable design stress for ring material	<b>ML<sup>-1</sup>T<sup>-2</sup></b>
<i>f<sub>s</sub></i>	Maximum allowable design stress for skirt material	<b>ML<sup>-1</sup>T<sup>-2</sup></b>

$f_t$	Maximum allowable design stress for tank material	$ML^{-1}T^{-2}$
$G$	Mean diameter of gasket	$L$
$g$	Gravitational acceleration	$LT^{-2}$
$H$	Total pressure force on flange	$MLT^{-2}$
$H_d$	Pressure force on area inside flange	$MLT^{-2}$
$H_g$	Gasket reaction	$MLT^{-2}$
$H_L$	Liquid depth	$L$
$H_p$	Height of local load above base	$L$
$H_t$	Pressure force on flange face	$MLT^{-2}$
$H_v$	Height (length) of cylindrical section between tangent lines	$L$
$h$	Height of domed head from tangent line	$L$
$h_c$	Initial displacement of shaft	$L$
$h_d$	Moment arm of force $H_d$	$L$
$h_g$	Moment arm of force $H_g$	$L$
$h_i$	Internal height of branch allowed as compensation	$L$
$h_o$	External height of branch allowed as compensation	$L$
$h_t$	Moment arm of force $H_t$	$L$
$I$	Second moment of area (moment of inertia)	$L^4$
$I'$	Second moment of area per unit length	$L^3$
$I_h$	Second moment of area of shell, horizontal vessel	$L^4$
$I_p$	Polar second moment of area	$L^4$
$I_r$	Second moment of area of ring	$L^4$
$I_v$	Second moment of area of vessel	$L^4$
$J$	Joint factor, welded joint	—
$K$	Ratio of diameters of thick cylinder = $D_o/D_i$	—
$K_c$	Collapse coefficient in equation 13.52	—
$L$	Unsupported length of vessel	$L$
$L'$	Effective length between stiffening rings	$L$
$L_c$	Critical distance between stiffening rings	$L$
$L_k$	Length of conical transition section	$L$
$L_o$	Distance between centre line of equipment and column	$L$
$L_r$	Distance between edge of skirt to outer edge of flange	$L$
$M$	Bending moment	$ML^2T^{-2}$
$M_{atm}$	Moment acting on flange during bolting up	$ML^2T^{-2}$
$M_e$	Bending moment due to offset equipment	$ML^2T^{-2}$
$M_{L1}$	Longitudinal bending moment at mid-span	$ML^2T^{-2}$
$M_{L2}$	Longitudinal bending moment at saddle support	$ML^2T^{-2}$
$M_{op}$	Total moment acting on flange	$ML^2T^{-2}$
$M_s$	Bending moment at base of skirt	$ML^2T^{-2}$
$M_v$	Bending moment acting on vessel	$ML^2T^{-2}$
$M_x$	Bending moment at point $x$ from free end of column	$ML^2T^{-2}$
$M_1$	Bending moment acting along cylindrical sections	$ML^2T^{-2}$
$M_2$	Bending moment acting along diametrical sections	$ML^2T^{-2}$
$m_c$	Displaced mass, centrifuge	$M$
$N_b$	Number of bolts	—
$n$	Number of lobes	—
$P$	Pressure	$ML^{-1}T^{-2}$
$P_c$	Critical buckling pressure	$ML^{-1}T^{-2}$
$P'_c$	Critical pressure to cause local buckling in a spherical shell	$ML^{-1}T^{-2}$
$P_d$	Design pressure	$ML^{-1}T^{-2}$
$P_e$	External pressure	$ML^{-1}T^{-2}$
$P_f$	Centrifugal pressure	$ML^{-1}T^{-2}$
$P_i$	Internal pressure	$ML^{-1}T^{-2}$
$P_m$	Self-pressure, centrifuge	$ML^{-1}T^{-2}$
$P_t$	Total pressure acting on centrifuge wall	$ML^{-1}T^{-2}$
$P_w$	Wind pressure loading	$ML^{-1}T^{-2}$
$\Delta P'$	Effective tube-plate design pressure difference	$ML^{-1}T^{-2}$
$p_b$	Bolt pitch	$L$



$p_h$	Hole pitch	L
$R_c$	Crown radius	L
$R_k$	Knuckle radius	L
$R_i$	Radius of interface	L
$R_o$	Major radius of torus	L
$R_p$	Radius of curvature of plate	L
$R_s$	Outside radius of sphere	L
$R_1$	Inside radius of centrifuge bowl	L
$R_2$	Radius of liquid surface	L
$r$	Radius	L
$r_1$	Meridional radius of curvature	L
$r_2$	Circumferential radius of curvature	L
$s$	Resisting force per unit displacement	MT <sup>-2</sup>
$T$	Torque	ML <sup>2</sup> T <sup>-2</sup>
$t$	Thickness of plate (shell)	L
$t_b$	Thickness of base ring	L
$t_c$	Thickness of bracket plate	L
$t_f$	Thickness of flange	L
$t_n$	Actual thickness of branch	L
$t_p$	Tube-plate thickness	L
$t_s$	Skirt thickness	L
$u_w$	Wind velocity	LT <sup>-1</sup>
$W$	Total weight of vessel and contents	MLT <sup>-2</sup>
$W_e$	Weight of ancillary equipment	MLT <sup>-2</sup>
$W_m$	Greater value of $W_{m1}$ and $W_{m2}$ in equation 13.109	MLT <sup>-2</sup>
$W_{m1}$	Minimum bolt load required under operating conditions	MLT <sup>-2</sup>
$W_{m2}$	Minimum bolt load required to seal gasket	MLT <sup>-2</sup>
$W_v$	Weight of vessel	MLT <sup>-2</sup>
$w$	Deflection of flat plate	L
$w$	Loading per unit length	MT <sup>-2</sup>
$x$	Radius from centre of flat plate to point of interest	L
$x$	Distance from free end of cantilever beam	L
$x_c$	Displacement caused by centrifugal force	L
$y$	Minimum seating pressure for gasket	ML <sup>-1</sup> T <sup>-2</sup>
$\alpha$	Cone half cone apex angle	—
$\Delta$	Dilation	L
$\Delta_c$	Dilation of cylinder	L
$\Delta_s$	Dilation of sphere	L
$\varepsilon$	Strain	—
$\varepsilon_1, \varepsilon_2$	Principal strains	—
$\theta$	Angle	—
$\theta_s$	Base angle of conical section	—
$\lambda$	Ligament efficiency	—
$\nu$	Poisson's ratio	—
$\rho_m$	Density of vessel material	ML <sup>-3</sup>
$\rho_a$	Density of air	ML <sup>-3</sup>
$\rho_L$	Liquid density	ML <sup>-3</sup>
$\rho_{L1}$	Density of heavier liquid	ML <sup>-3</sup>
$\rho_{L2}$	Density of lighter liquid	ML <sup>-3</sup>
$\sigma$	Normal stress	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_b$	Bending stress	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_{b1}$	Bending stress at mid-span	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_{b2}$	Bending stress at saddle supports	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_e$	Stress at elastic limit of material	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma'_e$	Elastic limit stress divided by factor of safety	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_h$	Circumferential (hoop) stress	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_{hb}$	Longitudinal hub stress	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_L$	Longitudinal stress	ML <sup>-1</sup> T <sup>-2</sup>
$\sigma_r$	Radial stress	ML <sup>-1</sup> T <sup>-2</sup>

$\sigma_{rd}$	Radial flange stress	$ML^{-1}T^{-2}$
$\sigma_s$	Stress in skirt support	$ML^{-1}T^{-2}$
$\sigma_t$	Tangential (hoop) stress	$ML^{-1}T^{-2}$
$\sigma_{tg}$	Tangential flange stress	$ML^{-1}T^{-2}$
$\sigma_{ws}$	Stress in skirt due to weight of vessel	$ML^{-1}T^{-2}$
$\sigma_x$	Normal stress in $x$ direction	$ML^{-1}T^{-2}$
$\sigma_y$	Normal stress in $y$ direction	$ML^{-1}T^{-2}$
$\sigma_z$	Axial stresses in vessel	$ML^{-1}T^{-2}$
$\sigma_1, \sigma_2, \sigma_3$	Principal stresses	$ML^{-1}T^{-2}$
$\tau$	Torsional shear stress	$ML^{-1}T^{-2}$
$\tau_{xy}$	Shear stress	$ML^{-1}T^{-2}$
$\tau_1, \tau_2, \tau_3$	Shear stress maxima	$ML^{-1}T^{-2}$
$\phi$	Slope of flat plate	—
$\phi$	Angle	—
$\omega$	Rotational speed	$T^{-1}$
<i>Superscript</i>		
$\wedge$	Maximum	

### 13.20. PROBLEMS

**13.1.** Calculate the maximum membrane stress in the wall of shells having the shapes listed below. The vessel walls are 2 mm thick and subject to an internal pressure of 5 bar.

1. An infinitely long cylinder, inside diameter 2 m.
2. A sphere, inside diameter 2 m.
3. An ellipsoid, major axis 2 m, minor axis 1.6 m.
4. A torus, mean diameter 2 m, diameter of cylinder 0.3 m.

**13.2.** Compare the thickness required for a 2 m diameter flat plate, designed to resist a uniform distributed load of  $10 \text{ kN/m}^2$ , if the plate edge is:

- (a) completely rigid,
- (b) free to rotate.

Take the allowable design stress for the material as  $100 \text{ MN/m}^2$  and Poisson's ratio for the material as 0.3.

**13.3.** A horizontal, cylindrical, tank, with hemispherical ends, is used to store liquid chlorine at 10 bar. The vessel is 4 m internal diameter and 20 m long. Estimate the minimum wall thickness required to resist this pressure, for the cylindrical section and the heads. Take the design pressure as 12 bar and the allowable design stress for the material as  $110 \text{ MN/m}^2$ .

**13.4.** The thermal design of a heat exchanger to recover heat from a kerosene stream by transfer to a crude oil stream was carried in Chapter 12, Example 12.2. Make a preliminary mechanical design for this exchanger. Base your design on the specification obtained from the CAD design procedure used in the example. All material of construction to be carbon steel (semi-killed or silicon killed). Your design should cover:

- (a) choice of design pressure and temperature,
- (b) choice of the required corrosion allowances,

- (c) choice of the type of end covers,
- (d) determination of the minimum wall thickness for the shell, headers and ends,
- (e) a check on the pressure rating of the tubes,
- (f) a suggested thickness for the tube sheets—detailed stressing is not required,
- (g) selection the flange types and dimensions—use standard flanges,
- (h) design of the exchanger supports.

**13.5.** Make a preliminary mechanical design for the vertical thermosyphon reboiler for which the thermal design was done as Example 12.9 in Chapter 12. The inlet liquid nozzle and the steam connections will be 50 mm inside diameter. Flat plate end closures will be used on both headers. The reboiler will be hung from four bracket supports, positioned 0.5 m down from the top tube plate. The shell and tubes will be of semi-killed carbon steel.

Your design should cover:

- (a) choice of design pressure and temperature,
- (b) choice of the required corrosion allowances,
- (c) selection of the header dimensions.
- (d) determination of the minimum wall thickness for the shell, headers and ends,
- (e) a check on the pressure rating of the tubes,
- (f) a suggested thickness for the tube sheets—detailed stressing is not required,
- (g) selection the flanges types and dimensions—use standard flanges,
- (h) reinforcement at the nozzles, if required,
- (i) design of the exchanger support brackets.

**13.6.** The specification for of a sieve plate column is given below. Make a preliminary mechanical design for the column. You design should include:

- (a) column wall thickness,
- (b) selection and sizing of vessel heads,
- (c) reinforcement, if any, of openings,
- (d) the nozzles and flanges (use standard flanges),
- (e) column supporting skirt and base ring/flange.

You need not design the plates or plate supports.

You should consider the following design loads:

- (a) internal pressure,
- (b) wind loading,
- (c) dead weight of vessel and contents (vessel full of water).

There will be no significant loading from piping and external equipment. Earthquake loading need not be considered.

Column specification:

Length of cylindrical section 37 m

Internal diameter 1.5 m

Heads, standard ellipsoidal

50 sieve plates

Nozzles: feed, at mid-point, 50 mm inside diameter,

vapour out, 0.7 m below top of cylindrical section, 250 mm

inside diameter

bottom product, centre of vessel head, 50 mm inside diameter

reflux return, 1.0 m below top of cylindrical section, 50 mm

inside diameter

Two 0.6 m diameter access ports (manholes) situated 1.0 m above the bottom and 1.5 m below the top of the column

Support skirt height 2.5 m

Access ladder with platforms

Insulation, mineral wool, 50 mm thick

Materials of construction: vessel stainless steel, unstabilised (304)

nozzles as vessel

skirt carbon steel, silicon killed

Design pressure 1200 kN/m<sup>2</sup>

Design temperature 150 °C

Corrosion allowance 2 mm.

Make a dimensioned sketch of your design and fill out the column specification sheet given in Appendix G.

- 13.7.** A jacketed vessel is to be used as a reactor. The vessel has an internal diameter of 2 m and is fitted with a jacket over a straight section 1.5 m long. Both the vessel and jacket walls are 25 mm thick. The spacing between the vessel and jacket is 75 mm.

The vessel and jacket are made of carbon steel. The vessel will operate at atmospheric pressure and the jacket will be supplied with steam at 20 bar. Check if the thickness of the vessel and jacket is adequate for this duty.

Take the allowable design stress as 100 N/mm<sup>2</sup> and the value of Young's modulus at the operating temperature as 180,000 N/mm<sup>2</sup>.

- 13.8.** A high pressure steam pipe is 150 mm inside diameter and 200 mm outside diameter. If the steam pressure is 200 bar, what will be the maximum shear stress in the pipe wall?

- 13.9.** A storage tank for concentrated nitric acid will be constructed from aluminium to resist corrosion. The tank is to have an inside diameter of 6 m and a height of 17 m. The maximum liquid level in the tank will be at 16 m. Estimate the plate thickness required at the base of the tank. Take the allowable design stress for aluminium as 90 N/mm<sup>2</sup>.

## *General Site Considerations*

### **14.1. INTRODUCTION**

In the discussion of process and equipment design given in the previous chapters no reference was made to the plant site. A suitable site must be found for a new project, and the site and equipment layout planned. Provision must be made for the ancillary buildings and services needed for plant operation; and for the environmentally acceptable disposal of effluent. These subjects are discussed briefly in this chapter.

### **14.2. PLANT LOCATION AND SITE SELECTION**

The location of the plant can have a crucial effect on the profitability of a project, and the scope for future expansion. Many factors must be considered when selecting a suitable site, and only a brief review of the principal factors will be given in this section. Site selection for chemical process plants is discussed in more detail by Merims (1966) and Mecklenburgh (1985); see also AIChE (2003). The principal factors to consider are:

1. Location, with respect to the marketing area.
2. Raw material supply.
3. Transport facilities.
4. Availability of labour.
5. Availability of utilities: water, fuel, power.
6. Availability of suitable land.
7. Environmental impact, and effluent disposal.
8. Local community considerations.
9. Climate.
10. Political and strategic considerations.

#### ***Marketing area***

For materials that are produced in bulk quantities; such as cement, mineral acids, and fertilisers, where the cost of the product per tonne is relatively low and the cost of transport a significant fraction of the sales price, the plant should be located close to the primary market. This consideration will be less important for low volume production, high-priced products; such as pharmaceuticals.

In an international market, there may be an advantage to be gained by locating the plant within an area with preferential tariff agreements; such as the European Community (EC).

### ***Raw materials***

The availability and price of suitable raw materials will often determine the site location. Plants producing bulk chemicals are best located close to the source of the major raw material; where this is also close to the marketing area.

### ***Transport***

The transport of materials and products to and from the plant will be an overriding consideration in site selection.

If practicable, a site should be selected that is close to at least two major forms of transport: road, rail, waterway (canal or river), or a sea port. Road transport is being increasingly used, and is suitable for local distribution from a central warehouse. Rail transport will be cheaper for the long-distance transport of bulk chemicals.

Air transport is convenient and efficient for the movement of personnel and essential equipment and supplies, and the proximity of the site to a major airport should be considered.

### ***Availability of labour***

Labour will be needed for construction of the plant and its operation. Skilled construction workers will usually be brought in from outside the site area, but there should be an adequate pool of unskilled labour available locally; and labour suitable for training to operate the plant. Skilled tradesmen will be needed for plant maintenance. Local trade union customs and restrictive practices will have to be considered when assessing the availability and suitability of the local labour for recruitment and training.

### ***Utilities (services)***

Chemical processes invariably require large quantities of water for cooling and general process use, and the plant must be located near a source of water of suitable quality. Process water may be drawn from a river, from wells, or purchased from a local authority.

At some sites, the cooling water required can be taken from a river or lake, or from the sea; at other locations cooling towers will be needed.

Electrical power will be needed at all sites. Electrochemical processes that require large quantities of power; for example, aluminium smelters, need to be located close to a cheap source of power.

A competitively priced fuel must be available on site for steam and power generation.

### ***Environmental impact, and effluent disposal***

All industrial processes produce waste products, and full consideration must be given to the difficulties and cost of their disposal. The disposal of toxic and harmful effluents will

be covered by local regulations, and the appropriate authorities must be consulted during the initial site survey to determine the standards that must be met.

An environmental impact assessment should be made for each new project, or major modification or addition to an existing process, see Section 14.6.5.

### ***Local community considerations***

The proposed plant must fit in with and be acceptable to the local community. Full consideration must be given to the safe location of the plant so that it does not impose a significant additional risk to the community.

On a new site, the local community must be able to provide adequate facilities for the plant personnel: schools, banks, housing, and recreational and cultural facilities.

### ***Land (site considerations)***

Sufficient suitable land must be available for the proposed plant and for future expansion. The land should ideally be flat, well drained and have suitable load-bearing characteristics. A full site evaluation should be made to determine the need for piling or other special foundations.

### ***Climate***

Adverse climatic conditions at a site will increase costs. Abnormally low temperatures will require the provision of additional insulation and special heating for equipment and pipe runs. Stronger structures will be needed at locations subject to high winds (cyclone/hurricane areas) or earthquakes.

### ***Political and strategic considerations***

Capital grants, tax concessions, and other inducements are often given by governments to direct new investment to preferred locations; such as areas of high unemployment. The availability of such grants can be the overriding consideration in site selection.

## **14.3. SITE LAYOUT**

The process units and ancillary buildings should be laid out to give the most economical flow of materials and personnel around the site. Hazardous processes must be located at a safe distance from other buildings. Consideration must also be given to the future expansion of the site. The ancillary buildings and services required on a site, in addition to the main processing units (buildings), will include:

1. Storages for raw materials and products: tank farms and warehouses.
2. Maintenance workshops.
3. Stores, for maintenance and operating supplies.
4. Laboratories for process control.
5. Fire stations and other emergency services.
6. Utilities: steam boilers, compressed air, power generation, refrigeration, transformer stations.

7. Effluent disposal plant.
8. Offices for general administration.
9. Canteens and other amenity buildings, such as medical centres.
10. Car parks.

When roughing out the preliminary site layout, the process units will normally be sited first and arranged to give a smooth flow of materials through the various processing steps, from raw material to final product storage. Process units are normally spaced at least 30 m apart; greater spacing may be needed for hazardous processes.

The location of the principal ancillary buildings should then be decided. They should be arranged so as to minimise the time spent by personnel in travelling between buildings. Administration offices and laboratories, in which a relatively large number of people will be working, should be located well away from potentially hazardous processes. Control rooms will normally be located adjacent to the processing units, but with potentially hazardous processes may have to be sited at a safer distance.

The siting of the main process units will determine the layout of the plant roads, pipe alleys and drains. Access roads will be needed to each building for construction, and for operation and maintenance.

Utility buildings should be sited to give the most economical run of pipes to and from the process units.

Cooling towers should be sited so that under the prevailing wind the plume of condensate spray drifts away from the plant area and adjacent properties.

The main storage areas should be placed between the loading and unloading facilities and the process units they serve. Storage tanks containing hazardous materials should be sited at least 70 m (200 ft) from the site boundary.

A typical plot plan is shown in Figure 14.1.

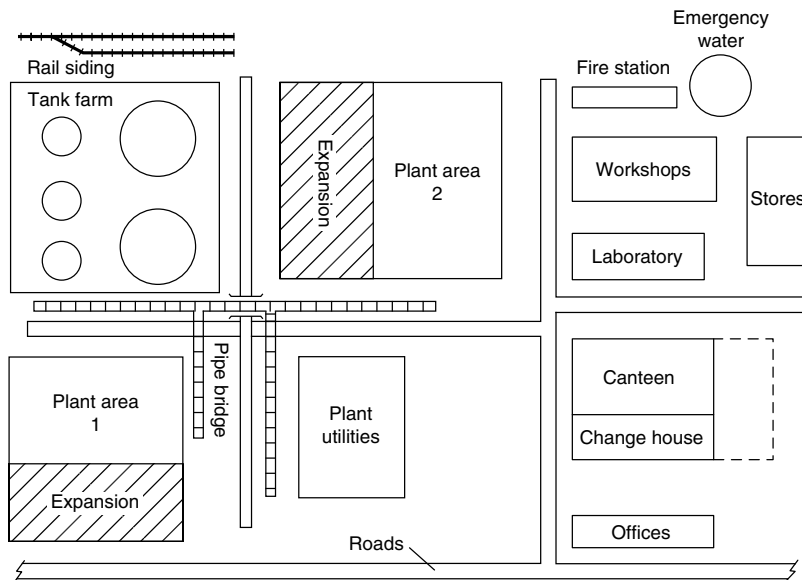


Figure 14.1. A typical site plan



A comprehensive discussion of site layout is given by Mecklenburgh (1985); see also House (1969), Kaess (1970) and Meissner and Shelton (1992).

## 14.4. PLANT LAYOUT

The economic construction and efficient operation of a process unit will depend on how well the plant and equipment specified on the process flow-sheet is laid out.

A detailed account of plant layout techniques cannot be given in this short section. A fuller discussion can be found in the book edited by Mecklenburgh (1985) and in articles by Kern (1977, 1978), Meissner and Shelton (1992), Brandt *et al.* (1992), and Russo and Tortorella (1992).

The principal factors to be considered are:

1. Economic considerations: construction and operating costs.
2. The process requirements.
3. Convenience of operation.
4. Convenience of maintenance.
5. Safety.
6. Future expansion.
7. Modular construction.

### **Costs**

The cost of construction can be minimised by adopting a layout that gives the shortest run of connecting pipe between equipment, and the least amount of structural steel work. However, this will not necessarily be the best arrangement for operation and maintenance.

### **Process requirements**

An example of the need to take into account process considerations is the need to elevate the base of columns to provide the necessary net positive suction head to a pump (see Chapter 5) or the operating head for a thermosyphon reboiler (see Chapter 12).

### **Operation**

Equipment that needs to have frequent operator attention should be located convenient to the control room. Valves, sample points, and instruments should be located at convenient positions and heights. Sufficient working space and headroom must be provided to allow easy access to equipment.

### **Maintenance**

Heat exchangers need to be sited so that the tube bundles can be easily withdrawn for cleaning and tube replacement. Vessels that require frequent replacement of catalyst or packing should be located on the outside of buildings. Equipment that requires dismantling for maintenance, such as compressors and large pumps, should be placed under cover.

## ***Safety***

Blast walls may be needed to isolate potentially hazardous equipment, and confine the effects of an explosion.

At least two escape routes for operators must be provided from each level in process buildings.

## ***Plant expansion***

Equipment should be located so that it can be conveniently tied in with any future expansion of the process.

Space should be left on pipe alleys for future needs, and service pipes over-sized to allow for future requirements.

## ***Modular construction***

In recent years there has been a move to assemble sections of plant at the plant manufacturer's site. These modules will include the equipment, structural steel, piping and instrumentation. The modules are then transported to the plant site, by road or sea.

The advantages of modular construction are:

1. Improved quality control.
2. Reduced construction cost.
3. Less need for skilled labour on site.
4. Less need for skilled personnel on overseas sites.

Some of the disadvantages are:

1. Higher design costs.
2. More structural steel work.
3. More flanged connections.
4. Possible problems with assembly, on site.

A fuller discussion of techniques and applications of modular construction is given by Shelley (1990), Hesler (1990), and Whitaker (1984).

## ***General considerations***

Open, structural steelwork, buildings are normally used for process equipment; closed buildings are only used for process operations that require protection from the weather.

The arrangement of the major items of equipment will usually follow the sequence given on the process flow-sheet: with the columns and vessels arranged in rows and the ancillary equipment, such as heat exchangers and pumps, positioned along the outside. A typical preliminary layout is shown in Figure 14.2.

### **14.4.1. Techniques used in site and plant layout**

Cardboard cut-outs of the equipment outlines can be used to make trial plant layouts. Simple models, made up from rectangular and cylindrical blocks, can be used to study

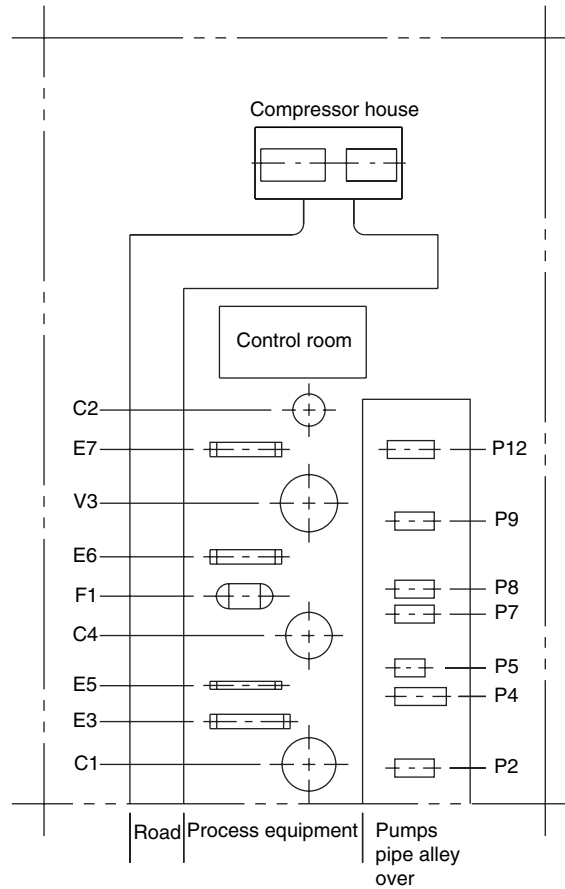


Figure 14.2. A typical plant layout

alternative layouts in plan and elevation. Cut-outs and simple block models can also be used for site layout studies. Once the layout of the major pieces of equipment has been decided, the plan and elevation drawings can be made and the design of the structural steel-work and foundations undertaken.

Large-scale models, to a scale of at least 1 : 30, are normally made for major projects. These models are used for piping design and to decide the detailed arrangement of small items of equipment, such as valves, instruments and sample points. Piping isometric diagrams are taken from the finished models. The models are also useful on the construction site, and for operator training. Proprietary kits of parts are available for the construction of plant models.

Computers are being increasingly used for plant layout studies, and computer models are complementing, if not yet replacing, physical models. Several proprietary programs are available for the generation of 3-dimensional models of plant layout and piping. Present systems allow designers to zoom in on a section of plant and view it from various angles. Developments of computer technology will soon enable engineers to

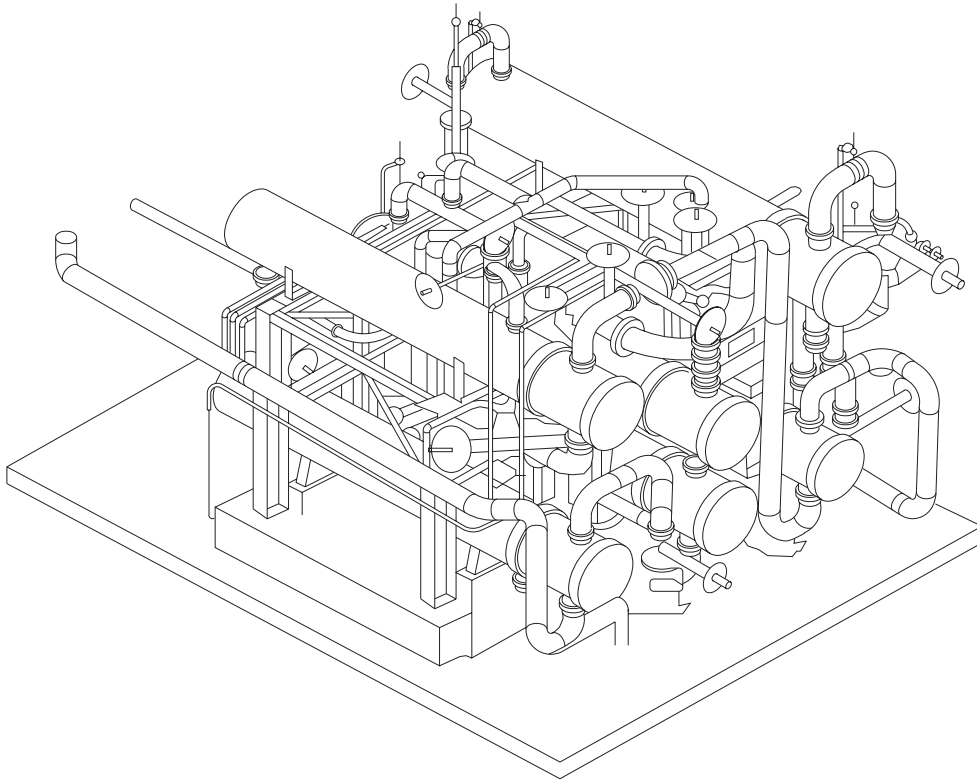


Figure 14.3. Computer generated layout “model” (Courtesy: Babcock Construction Ltd.)

virtually walk through the plant. A typical computer generated model is shown in Figure 14.3.

Some of the advantages of computer graphics modelling compared with actual scale models are:

1. The ease of electronic transfer of information. Piping drawings can be generated directly from the layout model. Bills of quantities: materials, valves, instruments, are generated automatically.
2. The computer model can be part of an integrated project information system, covering all aspects of the project from conception to operation.
3. It is easy to detect interference between pipe runs, and pipes and structural steel: occupying same space.
4. A physical model of a major plant construction can occupy several hundred square metres. The computer model is contained on a few discs.
5. The physical model has to be transported to the plant site for use in the plant construction and operator training. A computer model can be instantly available in the design office, the customer’s offices, and at the plant site.
6. Expert systems and optimisation programs can be incorporated in the package to assist the designer to find the best practical layout; see Madden *et al.* (1990).

## 14.5. UTILITIES

The word “Utilities” is now generally used for the ancillary services needed in the operation of any production process. These services will normally be supplied from a central site facility; and will include:

1. Electricity.
2. Steam, for process heating.
3. Cooling water.
4. Water for general use.
5. Demineralised water.
6. Compressed air.
7. Inert-gas supplies.
8. Refrigeration.
9. Effluent disposal facilities.

### ***Electricity***

The power required for electrochemical processes; motor drives, lighting, and general use, may be generated on site, but will more usually be purchased from the local supply company (the national grid system in the UK). The economics of power generation on site are discussed by Caudle (1975).

The voltage at which the supply is taken or generated will depend on the demand. For a large site the supply will be taken at a very high voltage, typically 11,000 or 33,000 V. Transformers will be used to step down the supply voltage to the voltages used on the site. In the United Kingdom a three-phase 415-V system is used for general industrial purposes, and 240-V single-phase for lighting and other low-power requirements. If a number of large motors is used, a supply at an intermediate high voltage will also be provided, typically 6000 or 11,000 V.

A detailed account of the factors to be considered when designing electrical distribution systems for chemical process plants, and the equipment used (transformers, switch gear and cables), is given by Silverman (1964).

### ***Steam***

The steam for process heating is usually generated in water tube boilers; using the most economical fuel available. The process temperatures required can usually be obtained with low-pressure steam, typically 2.5 bar (25 psig), and steam is distributed at a relatively low mains pressure, typically around 8 bar (100 psig). Higher steam pressures, or proprietary heat-transfer fluids, such as Dowtherm (see Conant and Seifert, 1963), will be needed for high process temperatures. The generation, distribution and utilisation of steam for process heating in the manufacturing industries is discussed in detail by Lyle (1963).

### ***Combined heat and power (co-generation)***

The energy costs on a large site can be reduced if the electrical power required is generated on site and the exhaust steam from the turbines used for process heating. The overall

thermal efficiency of such systems can be in the range 70 to 80 per cent; compared with the 30 to 40 per cent obtained from a conventional power station, where the heat in the exhaust steam is wasted in the condenser. Whether a combined heat and power system scheme is worth considering for a particular site will depend on the size of the site, the cost of fuel, the balance between the power and heating demands; and particularly on the availability of, and cost of, standby supplies and the price paid for any surplus power electricity generated. The economics of combined heat and power schemes for chemical process plant sites in the United Kingdom is discussed by Grant (1979).

On any site it is always worth while considering driving large compressors or pumps with steam turbines and using the exhaust steam for local process heating.

### ***Cooling water***

Natural and forced-draft cooling towers are generally used to provide the cooling water required on a site; unless water can be drawn from a convenient river or lake in sufficient quantity. Sea water, or brackish water, can be used at coastal sites, but if used directly will necessitate the use of more expensive materials of construction for heat exchangers (see Chapter 7).

### ***Water for general use***

The water required for general purposes on a site will usually be taken from the local mains supply, unless a cheaper source of suitable quality water is available from a river, lake or well.

### ***Demineralised water***

Demineralised water, from which all the minerals have been removed by ion-exchange, is used where pure water is needed for process use, and as boiler feed-water. Mixed and multiple-bed ion-exchange units are used; one resin converting the cations to hydrogen and the other removing the acid radicals. Water with less than 1 part per million of dissolved solids can be produced.

### ***Refrigeration***

Refrigeration will be needed for processes that require temperatures below those that can be economically obtained with cooling water. For temperatures down to around 10°C chilled water can be used. For lower temperatures, down to -30°C, salt brines (NaCl and CaCl<sub>2</sub>) are used to distribute the "refrigeration" round the site from a central refrigeration machine. Vapour compression machines are normally used.

### ***Compressed air***

Compressed air will be needed for general use, and for the pneumatic controllers that are usually used for chemical process plant control. Air is normally distributed at a mains pressure of 6 bar (100 psig). Rotary and reciprocating single-stage or two-stage compressors are used. Instrument air must be dry and clean (free from oil).

### ***Inert gases***

Where large quantities of inert gas are required for the inert blanketing of tanks and for purging (see Chapter 9) this will usually be supplied from a central facility. Nitrogen is normally used, and is manufactured on site in an air liquefaction plant, or purchased as liquid in tankers.

### ***Effluent disposal***

Facilities will be required at all sites for the disposal of waste materials without creating a public nuisance; see Section 14.6.1.

## **14.6. ENVIRONMENTAL CONSIDERATIONS**

All individuals and companies have a duty of care to their neighbours, and to the environment in general. In the United Kingdom this is embodied in the Common Law. In addition to this moral duty, stringent controls over the environment are being introduced in the United Kingdom, the European Union, the United States, and in other industrialised countries and developing countries.

Vigilance is required in both the design and operation of process plant to ensure that legal standards are met and that no harm is done to the environment.

Consideration must be given to:

1. All emissions to land, air, water.
2. Waste management.
3. Smells.
4. Noise.
5. The visual impact.
6. Any other nuisances.
7. The environmental friendliness of the products.

### **14.6.1. Waste management**

Waste arises mainly as byproducts or unused reactants from the process, or as off-specification product produced through mis-operation. There will also be fugitive emissions from leaking seals and flanges, and inadvertent spills and discharges through mis-operation. In emergency situations, material may be discharged to the atmosphere through vents normally protected by bursting discs and relief valves.

The designer must consider all possible sources of pollution and, where practicable, select processes that will eliminate or reduce (minimise) waste generation. The Institution of Chemical Engineers has published a guide to waste minimisation, IChemE (1997).

Unused reactants can be recycled and off-specification product reprocessed. Integrated processes can be selected: the waste from one process becoming the raw material for another. For example, the otherwise waste hydrogen chloride produced in a chlorination process can be used for chlorination using a different reaction; as in the balanced, chlorination-oxyhydrochlorination process for vinyl chloride production. It may be

possible to sell waste to another company, for use as raw material in their manufacturing processes. For example, the use of off-specification and recycled plastics in the production of lower grade products, such as the ubiquitous black plastics bucket.

Processes and equipment should be designed to reduce the chances of mis-operation; by providing tight control systems, alarms and interlocks. Sample points, process equipment drains, and pumps should be sited so that any leaks flow into the plant effluent collection system, not directly to sewers. Hold-up systems, tanks and ponds, should be provided to retain spills for treatment. Flanged joints should be kept to the minimum needed for the assembly and maintenance of equipment.

When waste is produced, processes must be incorporated in the design for its treatment and safe disposal. The following techniques can be considered:

1. Dilution and dispersion.
2. Discharge to foul water sewer (with the agreement of the appropriate authority).
3. Physical treatments: scrubbing, settling, absorption and adsorption.
4. Chemical treatment: precipitation (for example, of heavy metals), neutralisation.
5. Biological treatment: activated sludge and other processes.
6. Incineration on land, or at sea.
7. Landfill at controlled sites.
8. Sea dumping – (now subject to tight international control).

A British Standard has been published to assist with the management of waste systems, BS EN ISO 14401 (1996).

The sources of air pollution and their control are covered in several books: Walk (1997), Heumann (1997), Davies (2000), and Cooper and Ally (2002).

### ***Gaseous wastes***

Gaseous effluents which contain toxic or noxious substances will need treatment before discharge into the atmosphere. The practice of relying on dispersion from tall stacks is seldom entirely satisfactory. Witness the problems with acid rain in Scandinavian countries attributed to discharges from power stations in the United Kingdom. Gaseous pollutants can be removed by absorption or adsorption. Finely dispersed solids can be removed by scrubbing, or using electrostatic precipitators; see Chapter 10. Flammable gases can be burnt. The subject of air pollution is covered by Strauss and Mainwarring (1984).

### ***Liquid wastes***

The waste liquids from a chemical process, other than aqueous effluent, will usually be flammable and can be disposed of by burning in suitably designed incinerators. Care must be taken to ensure that the temperatures attained in the incinerator are high enough to completely destroy any harmful compounds that may be formed; such as the possible formation of dioxins when burning chlorinated compounds. The gases leaving an incinerator may be scrubbed, and acid gases neutralised. A typical incinerator for burning gaseous or liquid wastes is shown in Chapter 3, Figure 3.16. The design of incinerators for hazardous waste and the problems inherent in the disposal of waste by incineration are discussed by Butcher (1990) and Baker-Counsell (1987).



In the past, small quantities of liquid waste, in drums, has been disposed of by dumping at sea or in land-fill sites. This is not an environmentally acceptable method and is now subject to stringent controls.

### **Solid wastes**

Solid waste can be burnt in suitable incinerators or disposed by burial at licensed land-fill sites. As for liquid wastes, the dumping of toxic solid waste at sea is now not acceptable.

### **Aqueous wastes**

The principal factors which determine the nature of an aqueous industrial effluent and on which strict controls will be placed by the responsible authority are:

1. pH.
2. Suspended solids.
3. Toxicity.
4. Biological oxygen demand.

The pH can be adjusted by the addition of acid or alkali. Lime is frequently used to neutralise acidic effluents.

Suspended solids can be removed by settling, using clarifiers (see Chapter 10).

For some effluents it will be possible to reduce the toxicity to acceptable levels by dilution. Other effluents will need chemical treatment.

The oxygen concentration in a water course must be maintained at a level sufficient to support aquatic life. For this reason, the biological oxygen demand of an effluent is of utmost importance. It is measured by a standard test: the BOD5 (five-day biological oxygen demand). This test measures the quantity of oxygen which a given volume of the effluent (when diluted with water containing suitable bacteria, essential inorganic salts, and saturated with oxygen) will absorb in 5 days, at a constant temperature of 20°C. The results are reported as parts of oxygen absorbed per million parts effluent (ppm). The BOD5 test is a rough measure of the strength of the effluent: the organic matter present. It does not measure the total oxygen demand, as any nitrogen compounds present will not be completely oxidised in 5 days. The Ultimate Oxygen Demand (UOD) can be determined by conducting the test over a longer period, up to 90 days. If the chemical composition of the effluent is known, or can be predicted from the process flow-sheet, the UOD can be estimated by assuming complete oxidation of the carbon present to carbon dioxide, and the nitrogen present to nitrate:

$$\text{UOD} = 2.67C + 4.57N$$

where C and N are the concentrations of carbon and nitrogen in ppm.

Activated sludge processes are frequently used to reduce the biological oxygen demand of an aqueous effluent before discharge.

A full discussion of aqueous effluent treatment is given by Eckenfelder *et al.* (1985); see also Eckenfelder (1999).

Where waste water is discharged into the sewers with the agreement of the local water authorities, a charge will normally be made according to the BOD value, and any treatment required. Where treated effluent is discharged to water courses, with the agreement of the appropriate regulatory authority, the BOD5 limit will typically be set at 20 ppm.

### **14.6.2. Noise**

Noise can cause a serious nuisance in the neighbourhood of a process plant. Care needs to be taken when selecting and specifying equipment such as compressors, air-cooler fans, induced and forced draught fans for furnaces, and other noisy plant. Excessive noise can also be generated when venting through steam and other relief valves, and from flare stacks. Such equipment should be fitted with silencers. Vendors' specifications should be checked to ensure that equipment complies with statutory noise levels; both for the protection of employees (see Chapter 9), as well as for noise pollution considerations. Noisy equipment should, as far as practicable, be sited well away from the site boundary. Earth banks and screens of trees can be used to reduce the noise level perceived outside the site.

### **14.6.3. Visual impact**

The appearance of the plant should be considered at the design stage. Few people object to the fairyland appearance of a process plant illuminated at night, but it is a different scene in daylight. There is little that can be done to change the appearance of a modern style plant, where most of the equipment and piping will be outside and in full view, but some steps can be taken to minimise the visual impact. Large equipment, such as storage tanks, can be painted to blend in with, or even contrast with, the surroundings. Landscaping and screening by belts of trees can also help improve the overall appearance of the site.

### **14.6.4. Legislation**

It is not feasible to review the growing body of legislation covering environmental control in this short chapter.

Stricter legislation and tighter control of discharges into the environment are being introduced in most countries. The specialist texts brought out by publishers catering for management topics, and by the government departments, should be consulted for up-to-date information on environmental legislation.

Legislation and control procedures in the United Kingdom are increasingly being derived from regulations promulgated by the European Union (EU).

Kiely (1996) gives a comprehensive summary of EU and US environmental legislation.

All the legislation embodies the concept of *Best Practicable Means* (BPM). This requires the designer to use the most appropriate treatment to comply with the regulation, whilst taking into account: local conditions, current technology and cost. The concept of BPM also applies to the installation, maintenance and operation of the plant.

### 14.6.5. Environmental auditing

An environmental audit is a systematic examination of how a business operation affects the environment. It will include all emissions to air, land, and water; and cover the legal constraints, the effect on community, the landscape, and the ecology. Products will be considered, as well as processes.

When applied at the design stage of a new development it is more correctly called an *environmental impact assessment*.

The aim of the audit or assessment is to:

1. Identify environmental problems associated with manufacturing process and the use of the products, before they become liabilities.
2. To develop standards for good working practices.
3. To provide a basis for company policy.
4. To ensure compliance with environmental legislation.
5. To satisfy requirements of insurers.
6. To be seen to be concerned with environmental questions: important for public relations.
7. To minimise the production of waste: an economic factor.

Environmental auditing is discussed by Grayson (1992). His booklet is a good source of references for commentary on the subject, and to government bulletins.

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 (May 23rd) 130. How to manage plant design to obtain minimum costs.  
 (July 4th) 123. Specifications are the key to successful plant design.  
 (Aug. 15th) 153. Layout arrangements for distillation columns.  
 (Sept. 12th) 169. How to find optimum layout for heat exchangers.  
 (Nov. 7th) 93. Arrangement of process and storage vessels.  
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(Feb. 27th) 117. Space requirements and layout for process furnaces.  
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APPENDIX A

# Graphical Symbols for Piping Systems and Plant

BASED ON BS 1553: PART 1: 1977

## Scope

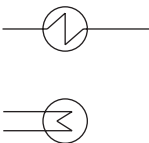
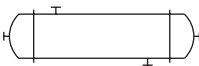
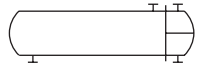
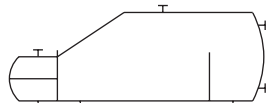
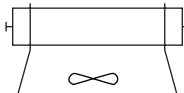
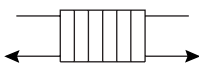
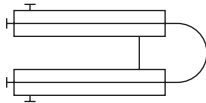
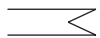
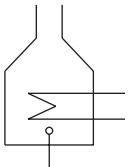
This part of BS 1553 specifies graphical symbols for use in flow and piping diagrams for process plant.

## **Symbols (or elements of symbols) for use in conjunction with other symbols**

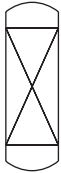
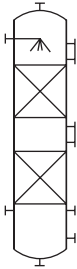
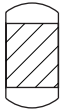
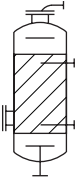
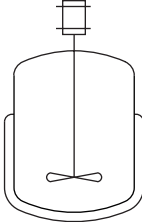
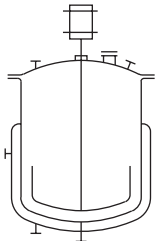
Mechanical linkage		Access point	
Weight device		Equipment branch: general symbol Note. The upper representation does not necessarily imply a flange, merely the termination point. Where a breakable connection is required the branch/pipe would be as shown in the lower symbol	
Electrical device		Equipment penetration (fixed)	
Vibratory or loading device (any type)		Equipment penetration (removable)	
Spray device		Boundary line	
Rotary movement		Point of change	
Stirring device		Discharge to atmosphere	
Fan			

**Basic and developed symbols for plant and equipment**



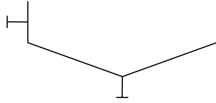
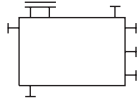
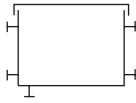
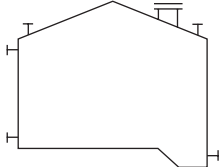
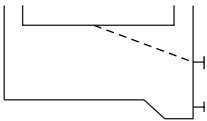
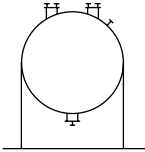
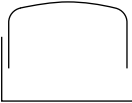
Heat transfer equipment

<p>Heat exchanger (basic symbols)</p> <p>Alternative:</p>	
<p>Shell and tube: fixed tube sheet</p>	
<p>Shell and tube: U tube or floating head</p>	
<p>Shell and tube: kettle reboiler</p>	
<p>Air - blown cooler</p>	
<p>Plate type</p>	
<p>Double pipe type</p>	
<p>Heating/cooling coil (basic symbol)</p>	
<p>Fired heater/boiler (basic symbol)</p>	


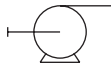
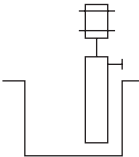

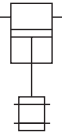
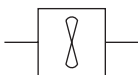
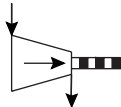
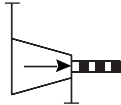

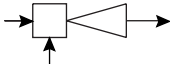


<p>Fluid contacting vessel (basic symbol)</p>	
<p>Fluid contacting vessel Support grids and distribution details may be shown</p>	
<p>Reaction or absorption vessel (basic symbol)</p>	
<p>Reaction or absorption vessel Where it is necessary to show more than one layer of material alternative hatching should be used</p>	
<p>Autoclave (basic symbol)</p>	
<p>Autoclave</p>	







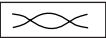
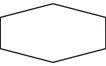


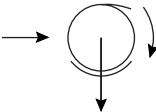



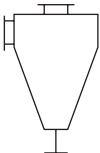

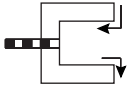

Open tank (basic symbol)	
Open tank	
Clarifier or settling tank	
Sealed tank	
Covered tank	
Tank with fixed roof (with draw-off sump)	
Tank with floating roof (with roof drain)	
Storage sphere	
Gas holder (basic symbol for all types)	

Pumps and compressors

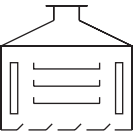
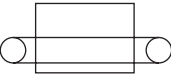
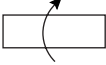
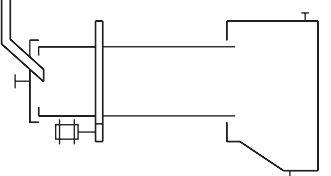
<p>Rotary pump, fan or simple compressor (basic symbol)</p>	
<p>Centrifugal pump or centrifugal fan</p>	
<p>Centrifugal pump (submerged suction)</p>	
<p>Positive displacement rotary pump or rotary compressor</p>	
<p>Positive displacement pump (reciprocating)</p>	
<p>Axial flow fan</p>	
<p>Compressor: centrifugal / axial flow ( basic symbol )</p>	
<p>Compressor: centrifugal / axial flow</p>	
<p>Compressor: reciprocating ( basic symbol )</p>	
<p>Ejector / injector ( basic symbol )</p>	

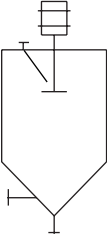
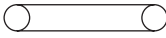
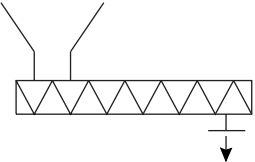

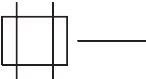
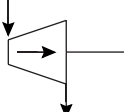
## Solids handling

Size reduction	
Breaker gyratory	
Roll crusher	
Pulverizer : ball mill	
Mixing (basic symbol)	
Kneader	
Ribbon blender	
Double cone blender	
Filter (basic symbol, simple batch)	
Filter press (basic symbol)	
Rotary filter, film drier or flaker	

Cyclone and hydroclone (basic symbol)	
Cyclone and hydroclone	
Centrifuge (basic symbol)	
Centrifuge: horizontal peeler type	
Centrifuge: disc bowl type	

Drying

Drying oven	
Belt drier (basic symbol)	
Rotary drier (basic symbol)	
Rotary kiln	

Spray drier	
<b>Materials handling</b>	
Belt conveyor	
Screw conveyor	
Elevator (basic symbol)	
<b>Prime movers</b>	
Electric motor (basic symbol)	
Turbine (basic symbol)	

## APPENDIX B

# *Corrosion Chart*

An R indicates that the material is resistant to the named chemical up to the temperature shown, subject to the limitations given in the notes. The notes are given at the end of the table.

A *blank* indicates that the material is unsuitable. ND indicates that no data was available for the particular combination of material and chemical.

This chart is reproduced with the permission of IPC Industrial Press Ltd.

### **NOTE**

This appendix should be used as a guide only—  
before a material is used its suitability should be  
cross-checked with the manufacturer.

METALS										
	Aluminium (a)	Aluminium Bronze	Brass (b)	Cast Iron (c)	Copper	Gunmetal and Bronze (d)	High Si Iron (14% Si) (e)	Lead	Mild Steel BSS 15	Nickel (cast)
Centigrade	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°
Acetaldehyde	R R R	R R R	R R R	R ND ND	R R R	R R R	R R R	R ND	No data	R R R
Acetic acid (10%)	R R	R R R			R R R	R R R	R R R	R ND		R <sup>20</sup> R R
Acetic acid (glac. & anh.)	R <sup>1</sup> R R	R R R			R R R	R R R	R R R	R ND		R R R
Acetic anhydride	R <sup>1</sup> R R	R R R		R R R	R R R	R R	R R R			R R R
Acetone	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R <sup>11</sup>	R R R
Other ketones	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	No data	R R R
Acetylene	R R R		R R R <sup>82</sup>	R R R				R R R	R R R	R R R
Acid fumes	R <sup>2</sup> R R	R <sup>2</sup> R <sup>2</sup> R <sup>2</sup>						R <sup>2</sup> R		
Alcohols (most fatty)	R <sup>1</sup> R R	R R R	R R R	R <sup>24</sup> R R	R R R	R R R	R R R	R R R	R R R	R R R
Aliphatic esters	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	No data	R R R
Alkyl chlorides	No data	No data		R <sup>11</sup> R R	R R R	R R R	R R R	R	R <sup>11</sup>	R R R
Alum	R R R	R R R			R R R	R R R	R R R	R R <sup>18</sup> R <sup>10</sup>		R
Aluminium chloride	R <sup>11</sup> ND ND	R <sup>20</sup> R <sup>20</sup>			R R R	R R R	R R	R <sup>4,10</sup>		
Ammonia, anhydrous	R R R	R R R		R	R R R <sup>83</sup>	R R R	R R R	R R R <sup>62</sup>	R R R	
Ammonia, aqueous	R R R			R R			R R R	R R	R R	
Ammonium chloride	R <sup>84</sup> R			R			R R R	R R R		R R R
Amyl acetate	R R R	R R R		R <sup>11</sup> R R	R R R	R R R	R R R	R <sup>4</sup> ND ND	No data	R R R
Aniline	R R R			R R R			R R R	R R	No data	R R R
Antimony trichloride		No data		R <sup>11</sup> R R	No data	R	R <sup>11</sup> R R	R <sup>4</sup> R		R <sup>11</sup> R R
Aqua regia										
Aromatic solvents	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R <sup>11</sup>	R R R
Beer	R R R	R R R	R R R	R R ND	R R R	R R R	R R ND			R R R
Benzoic acid	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>4</sup>		R R R
Boric acid	R R	R R R	R R R		R R R	R R R	R R R	R R R <sup>62</sup>		R R R
Brines, saturated	R R R	R R R		R <sup>84</sup>	R R R <sup>20</sup>	R R	R R R	R R		R R R
Bromine	R <sup>11</sup> R R	R <sup>20</sup>		R <sup>11</sup> R			R	R <sup>24</sup>		
Calcium chloride	R R R	R R R		R R	R R R	R R R	R R R	R <sup>4</sup>		R <sup>20</sup> R R
Carbon disulphide	R R R	R	R R R	R R R	R R R	R R R	R R R	R R R		R
Carbonic acid	R R R	R R R						R R R	ND	R
Carbon tetrachloride	R	R R R	R R R	R <sup>11</sup> R R	R R R	R R R	R R R	R R R <sup>11</sup>	R <sup>11</sup> R	R R R
Caustic soda & potash		R		R	R R R	R R R	R R R		R R	R R R
Chlorates of Na, K, Ba	R <sup>11</sup> R R	R R R			R R R	R R R	R R R	R R R		R R R
Chlorine, dry	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R <sup>4</sup>	R R R	R R R
Chlorine, wet							R R R	R R		
Chlorides of Na, K, Mg	R R R	R R R			R R R <sup>20</sup>	R R R	R R R	R <sup>4</sup> R <sup>4,22</sup>		R R R
Chloroacetic acids		No data			No data	No data			No data	R <sup>11</sup> R R
Chlorobenzene	R ND ND	R R R	No data	R R R	No data	R R R	R R R	R R	R <sup>11</sup> R	R R R
Chloroform	R <sup>1</sup> R R	R R R	R R R	R R	R R R	R R R	No data	R R	R <sup>11</sup> R	R R R
Chlorosulphonic acid		R <sup>20</sup> R <sup>20</sup> R <sup>20</sup>	No data	R <sup>11</sup> R R			R R	R <sup>4</sup>	R	
Chromic acid (80%)							R R	R R		
Citric acid	R R R	R R R			R R R	R R R	R R R	R R R <sup>25</sup>		R R R
Copper salts (most)		R R R				R R R	R <sup>16</sup> R R	R <sup>16</sup> R		R
Cresylic acids (50%)	R R R	R R R			R R R	R R R	R R R	R R R		R R R
Cyclohexane	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	No data	R R R
Detergents, synthetic	R R R	No data	R R R	No data	R R R	R R R	No data	R R	No data	R R R
Emulsifiers (all conc.)	R R R	R R R	No data	No data	R R R	No data	No data	R R	No data	No data
Ether	R <sup>1</sup> R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Fatty acids (> C <sub>6</sub> )	R R R	R R R			R R R	R R R	R R R	R <sup>4</sup> R R <sup>58</sup>		R R R
Ferric chloride							R	R <sup>4</sup>		
Ferrous sulphate		R <sup>20</sup> R <sup>20</sup> R <sup>20</sup>					R R R	R R R		
Fluorinated refrigerants, aerosols, e.g. Freon	R <sup>11</sup> ND ND	R R R	R R R	R R R	R R R	R R R	R R R	R R	R <sup>11</sup> ND ND	No data
Fluorine, dry	R R R	R R R <sup>11</sup>			R R R	R R R		R <sup>4</sup> R	R R R	R R R
Fluorine, wet				No data			R R R	R ND		R R R
Fluosilicic acid							R R R	R R <sup>58</sup>		R <sup>20</sup> R R
Formaldehyde (40%)	R	R R R	R	R	R R R	R R R	R R R	No data	R	R R R
Formic acid	R	R R R	No data		R R R	R R R	R R R	R <sup>30</sup> R <sup>36</sup>		R R R

METALS											
Nickel-Copper Alloys (e)	Ni-Resist (High Ni Iron) (c)	Platinum	Silver	Stainless Steel 18/8 (f)	Molybdenum Stainless Steel 18/8 (f)	Austenitic Ferritic Stainless Steel (x)	Tantalum	Tin (g)	Titanium	Zirconium	
20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	
R R R	R ND	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	R R R	
R R R	R	R R R	R R R	R R R	R R R	R R R	R R R	R	R R R	R R R	
R R R	R	R R R	R R R	R R	R R <sup>84</sup>	R R	R R	R R R	R R R	R R R	
R R R	R	R R R	R R R	R <sup>80</sup>	R R	R R R	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	
R <sup>2</sup> R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R ND ND	R R R	
R R R	R R R	R R R	R <sup>16</sup> R R	R R R	R R R	R R R	R R R	R <sup>44</sup> R R	R <sup>2</sup> R <sup>2</sup> R <sup>2</sup>	R <sup>2</sup> R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R	R <sup>93</sup> R <sup>93</sup> R <sup>93</sup>	R R R	
R R R	R R R	R R R	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R R R	R	R R R	R R R	
R R	R R	R R R	R R R	R R <sup>13</sup>	R R	R R	R R R	R	R R R	R R R	
R	R R R	R R R	R R R	R <sup>84</sup>	R <sup>84</sup> R	R <sup>84</sup> R	R R R	R <sup>57</sup>	R R R <sup>10</sup>	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	
R	R R R	R R R	R <sup>30</sup> R R	R R R	R R R	R R R	R R R	R <sup>13</sup>	R R R	R R R	
R R R	R R R	R R R	R <sup>73</sup> R R	R <sup>84</sup>	R <sup>84</sup> R	R	R R R	R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R	R R R	R R R	
R ND ND		R R R	R R R	R <sup>11</sup>	R <sup>11</sup> R <sup>11</sup>	R R	R R R	R	R R ND	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R ND	No data	
R R R	R R ND	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R ND	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	No data	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R <sup>42</sup>	R <sup>42</sup>	R <sup>42</sup>	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R <sup>42</sup>	R R R	R R R	R	R R R	R R R	
R R R	R R R	R R R	R R R	R R ND	R R ND	R R R	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R R R	R <sup>11</sup> R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R <sup>13</sup>	R R R <sup>13</sup>	R <sup>103</sup> R <sup>103</sup>	R <sup>10</sup> R R	R <sup>11</sup> R R	R R <sup>19</sup> R <sup>15</sup>	R R R	
R	R R R	R R R	R R R	R <sup>16</sup> R R	R <sup>16</sup> R R	R R R	R R R <sup>25</sup>	R R	R <sup>79</sup> R <sup>79</sup> R <sup>79</sup>	R <sup>25</sup> R <sup>25</sup> R <sup>25</sup>	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>91</sup> R R	
R R R	R R R	R R R	R <sup>70</sup> R R	R <sup>84</sup>	R <sup>84</sup> R	R <sup>56</sup> R <sup>56</sup>	R R R	R <sup>57</sup> R R	R R R	R R R	
R R R	ND ND ND	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R <sup>11</sup> R ND	R <sup>11</sup> R R	R R R	R R R	No data	No data	R R R	
R R R	R R R	R R R	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R R R	R <sup>11</sup> R R	R R ND	R R R	
R R		R <sup>30</sup> R R	R <sup>30</sup> R R	R R R	R <sup>84</sup>	No data	R R R	R R R	R R R	R R	
R R		R R R	R R R	R <sup>13</sup> R R	R R R <sup>13</sup>	R R R	R R R	R R R	R R R	R R <sup>19</sup>	
R		R R R	R <sup>30</sup> R R	R <sup>16</sup> R R	R <sup>16</sup> R R	R <sup>16</sup> R <sup>16</sup> R <sup>16</sup>	R R R	R R R	R R R	R <sup>16</sup> R R	
R R R	R ND ND	R R R	R R R	R R R	R R R	R R R	R R R	R	R ND ND	R R R	
R R R	No data	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R ND	R R R	
No data	No data	R R R	R R R	R R R	R R R	R R R	R R R	R	No data	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R ND	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	
R R	R	R R R	R R R	R R R	R R R	R R R	R R R		R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R R R	R R R	R R R	
R R R	No data	R R R	R R R	R ND ND	R ND ND	R R	R R		R <sup>5</sup> R R		
R R R	No data	R R R	R R R	R ND ND	R ND ND						
R R R	R <sup>32</sup> R <sup>32</sup> ND	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	R R R	
R R		R R R	R R R	R R R	R R R	R R R	R R R		R <sup>67</sup> R <sup>69</sup>	R <sup>10</sup> R <sup>20</sup>	



METALS										
	Aluminium (a)	Aluminium Bronze	Brass (b)	Cast Iron (c)	Copper	Gunmetal and Bronze (d)	High Si Iron (14% Si) (c)	Lead	Mild Steel BSS 15	Nickel (cast)
Centigrade	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°
Fruit juices	R R R	R R R			R R R	R R R	R R R		No data	R R R
Gelatine	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	No data	R R R
Glycerine	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R	R R R
Glycols	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R		R R R
Hexamine							R R R	R R	No data	R R R
Hydrazine	R ND ND			No data ND ND			No data	ND	R R R	R ND ND
Hydrobromic acid (50%)										
Hydrochloric acid (10%)		R								
Hydrochloric acid (conc.)		R <sup>62</sup>						R R	R <sup>4,11</sup>	R
Hydrocyanic acid	R R R	R <sup>20</sup> R <sup>20</sup> R <sup>20</sup>						R R R	R R	R R R
Hydrofluoric acid (40%)		R <sup>62</sup>							R	R <sup>20</sup>
Hydrofluoric acid (75%)		R <sup>62</sup>								R
Hydrogen peroxide (30%) (30-90%)	R R R R R R							R		R
Hydrogen sulphide	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R R R	R <sup>4,34,76</sup>	R <sup>11</sup> R R
Hypochlorites		R					R R R	R R R		R <sup>11</sup> R R
Lactic acid (100%)	R R R	R R		No data	R R	R <sup>4</sup> R <sup>4</sup>	R R R	ND		R R R
Lead acetate	R <sup>11</sup> R R	No data		No data	R R R	R R R	R R R	R <sup>4</sup>	R <sup>11</sup> R R	R R R
Lime (CaO)	R <sup>11</sup>	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>4</sup>	R <sup>11</sup> R R	R R R
Maleic acid	R R R	No data	No data		R R R	No data	R R ND		No data	R R R
Meat juices	R R R	R R R		No data			No data	No data	No data	No data
Mercuric chloride								R		
Mercury				R R R				R R R		R <sup>27</sup> R R
Milk & its products	R R R	R R R		No data		R R R	No data			R R R
Moist air	R R R	R R R			R R R	R R R	R R R	R R R		R R R
Molasses	R R R	R <sup>30</sup> R <sup>30</sup> R <sup>30</sup>	R <sup>30</sup> R	R R R	R <sup>30</sup> R R	R <sup>30</sup> R R	R R R		No data	R R R
Naphtha	R R R	R R R	R R R	R R R	R R R	R R R	No data	R R	R	R
Naphthalene	R R R	No data	No data	R R R	R R R	No data	R R R	R R	R	R R R
Nickel salts		No data		No data		R R R	R R R	R R		R <sup>40</sup> R R
Nitrates of Na, K, NH <sub>3</sub>	R R R	R <sup>73</sup> R <sup>73</sup> R <sup>73</sup>		R <sup>11</sup> R R			R R R	R R R		R R R
Nitric acid (<25%)								R		
Nitric acid (50%)								R R R		
Nitric acid (95%)	R R R							R R R		
Nitric acid, fuming	R ND ND							R R R		R
Oils, essential	R R R	R R R	R R R	R R R	R R R	R R R	R R R	No data	R R	R R R
Oils, mineral	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R	R R R
Oils, vegetable & animal	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R	R R R
Oxalic acid	R <sup>50</sup>	R R R	No data				R R R	R <sup>4</sup>		
Ozone	R R R	No data	No data	R ND ND	No data	No data	R R R	No data	R <sup>11</sup> R R	No data
Paraffin wax	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R ND	R R	R R R
Perchloric acid			No data				R R R	R R R		
Phenol	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>4</sup> R R <sup>19</sup>	No data	R R R
Phosphoric acid (25%)	R	R R R			R R R		R R R	R R R		
Phosphoric acid (50%)		R R R					R R R	R R R		
Phosphoric acid (95%)		R R R					R R R	R R		
Phosphorus chlorides		R <sup>11</sup> R <sup>11</sup> R <sup>11</sup>		R <sup>11</sup> R			R R R <sup>11</sup>	R R R	R <sup>11</sup> R R	R R R
Phosphorus pentoxide	R <sup>11</sup> ND ND	No data					R R R	R R R	R <sup>11</sup> R R	No data
Phthalic acid	R R R	R R R	No data		R R R	R R R	R R R	R R	No data	R R R
Picric acid	R ND ND						R R R	R <sup>4</sup>		R <sup>11</sup>
Pyridine	R R R	No data		R R R			R R R	R R	No data	R R R
Sea water	R R R	R R R	R <sup>62</sup> R R	R <sup>84</sup>	R R R	R R R	R R R	R R		R ND ND
Silicic acid	R R R		No data		R R R	No data	R R ND	R R	No data	R R ND
Silicone fluids	R R R	R R R		R R R	R R R	R R R	No data	R R R	No data	R R R
Silver nitrate				ND ND				R R R		
Sodium carbonate	R <sup>42</sup> R	R R R <sup>4</sup>	R R R	R <sup>11</sup> R R	R R R	R R R	R R R	R <sup>4</sup>	R R R	R R R
Sodium peroxide				R <sup>10</sup> R R			R <sup>10</sup> R <sup>10</sup>			R R R



METALS										
	Aluminium (a)	Aluminium Bronze	Brass (b)	Cast Iron (c)	Copper	Gunmetal and Bronze (d)	High Si Iron (14% Si) (c)	Lead	Mild Steel BSS 15	Nickel (cast)
Centigrade	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°
Sodium silicate	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sodium sulphide	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Stannic chloride	R R R	R <sup>11</sup>	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Starch	R R R	R R R	No data	R R R	R R R	R R R	R R R	No data	No data	R R R
Sugar, syrups, jams	R R R	R R R	R R R	R R ND	R R R	R R R	R R R	No data	No data	R R R
Sulphamic acid	R <sup>50</sup>	No data	R R R	R R R	R R R	R R R	R R R	R R R	No data	No data
Sulphates (Na, K, Mg, Ca)	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphites	R R R	R R R	R R R	R <sup>38</sup> R R	R R R	R R R	R <sup>38</sup> R	R R R	R R R	R R R
Sulphonic acids	No data	No data	No data	R <sup>11</sup>	No data	No data	R R R	R R R	No data	No data
Sulphur	R R R	R R R	R R R	R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphur dioxide, dry	R R R	R R R	R R R	R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphur dioxide, wet	R <sup>4</sup> R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphur trioxide	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R <sup>11</sup> R R	R <sup>11</sup> R R	R R R	R R R	R <sup>11</sup> R R	R R R
Sulphuric acid (< 50%)	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphuric acid (70%)	R R R	R <sup>62</sup>	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphuric acid (95%)	R R R	R <sup>62</sup>	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphuric acid, fuming	R <sup>4</sup>	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Sulphur chlorides	R R R	R R R	R R R	R <sup>11</sup> R <sup>11</sup>	R R R	R R R	No data	R <sup>4</sup>	No data	No data
Tallow	R R R	R R R	No data	R R R	R R R	R R R	R R R	R R R	No data	No data
Tannic acid (10%)	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R ND ND
Tartaric acid	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>4</sup> R R	R R R	R <sup>20</sup> R R
Trichlorethylene	R R R	R R R	R R R	R R R	R R R	R R R	R R ND	R R R	R <sup>11</sup> R	R R R
Vinegar	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Water, distilled	R R R	R <sup>53</sup> R	R R R	R R R	R <sup>53</sup> R	R <sup>53</sup> R R	R R R	R <sup>53</sup> R R	R <sup>53</sup> R R	R R R
Water, soft	R <sup>43</sup> R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>53</sup> R R	R R R
Water, hard	R <sup>43</sup> R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R
Yeast	R R R	No data	No data	R R R	R R R	R R R	R R R	No data	No data	R R R
Zinc chloride	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R <sup>4</sup> R	R R R	R <sup>20</sup> R R

METALS											
Nickel-Copper Alloys (e)	Ni Resist (High Ni Iron) (c)	Platinum	Silver	Stainless Steel 18/8 (f)	Molybdenum Stainless Steel 18/8 (f)	Austenitic Ferritic Stainless Steel (x)	Tantalum	Tin (g)	Titanium	Zirconium	
20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	
R R R No data	R R R R R R	R R R R R R	R R R R <sup>48</sup> R R	R R R R R	R R R R R	R R R R R	R R R R R R	R R R R R R	R R ND R ND R <sup>10</sup>	R R R R <sup>15</sup> R <sup>15</sup> R <sup>15</sup>	
R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R <sup>94</sup> R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R ND No data	R R R R R R	
R R R R	R <sup>20</sup> R R R	R R R R R R	R R R R R R	R R R R R R	R R <sup>37</sup> R R R	R R R R R	R R R R R R	R R R R R	R R R R ND R <sup>7</sup>	No data R R R	
R R R R R	R <sup>38</sup> R R No data	R R R R R R	R R R No data	R R R No data	R R R No data	R R R No data	R R R R R R	R R R R R R	No data R R R	R R R R R R	
R R R R	R R R R R R	R R R R R R	R R R R <sup>11</sup> R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R ND R R R	R R R R R R	
R R R	R R R R ND ND	R R R R R R	R R R R R R	R R R R	R R R R R	R R R R R	R R R R R R	R R R R R R	R R ND R R R	R R R R R R	
R R	R <sup>20</sup> R	R R R R R R	R R R R R R	R R <sup>80</sup>	R R <sup>80</sup> R	R R R	R R R R R R	R R R R R R	R <sup>49</sup> R R R <sup>78</sup> R	R R R R R R	
R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R	No data R R R	R R R R R R	
R R R R R R	R R R R R R	R R R R R R	R R <sup>70</sup> R R R R	R R R R <sup>11</sup> R R	R R R R <sup>11</sup> R R	R R R R R R	R R R R R R	R <sup>20</sup> R R R <sup>11</sup> R R	R R R <sup>19</sup> R R R	R R R R R R	
R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	
R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R <sup>84</sup> R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R R R R R R	
R R R No data	R R R R R R	R R R R R R	R R R R R R	R R R R R R	R <sup>84</sup> R R R R R	R R R R R R	R R R R R R	R <sup>57</sup> R R R R	R R R No data	R R R R R R	
R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R R <sup>52</sup>	R R R	













THERMOPLASTIC RESINS					THERMOSETTING RESINS				
Polyethylene Low Density	Polyethylene High Density	Polycarbonate Resins	Polypropylene	Polystyrene	Melamine Resins (o)	Furane Resin	Epoxy Resins (p)	Phenol Form- aldehyde Resins (f)	Polyester Resins
20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°
R R	R R	ND	R R R	No data	R	R R R	R R	R	R R R <sup>65</sup>
R R	R R	No data	R R R	No data	R	R R R	R R	No data	R R R <sup>65</sup>
R R	R R	No data	R <sup>7</sup> R R	No data	ND ND	R R ND	R <sup>68</sup>	R ND ND	No data
R R	R R	R ND	R R R	R R	R R	No data	R R	R R R	No data
R R	R R	R	R R ND	R R	R R	No data	R R	R R R	No data
ND ND	No data	No data	R R ND	No data	R ND ND	R ND ND	No data	No data	No data
R R	R R	R R ND	R R ND	R R	R R	R R R	R R <sup>30</sup>	R R R	R R <sup>30</sup> R <sup>65</sup>
R <sup>34</sup>	R R	No data	R R ND	R R	R R	R R R	R R	R R	R R <sup>30</sup> R <sup>65</sup>
No data	No data	No data	No data	No data	No data	R R ND	R R <sup>44</sup>	No data	No data
R R	R R	No data	R R ND	No data	R R	R R R	R R	No data	No data
R R	R R	No data	R R	R	R	R R R	R R	R ND ND	R ND ND
R	R R	ND	R R ND	R	R	R R R	R R	R ND ND	R <sup>30</sup> ND ND
R R	R R	ND	No data	R	R <sup>10</sup>	R R R	R <sup>11</sup>	R ND ND	R <sup>30</sup> ND ND
R R	R R	R R ND	R R	R	R	R R R	R R <sup>30</sup>	R R R	R <sup>30</sup> R
R R <sup>50</sup>	R R <sup>50</sup>	R R ND	R	R	R	R R R	R <sup>30</sup>	R R R	R <sup>30</sup> R
R <sup>50</sup>	R <sup>50</sup> R <sup>80</sup>	R <sup>60</sup>	R <sup>56</sup>	No data	ND ND	R R R	No data	R ND ND	No data
ND ND	No data		No data	No data	ND ND	R R R	No data	R ND ND	No data
R	R <sup>50</sup> ND ND	R ND	R R ND	R	R R	No data	R R	R R R	No data
R R	R <sup>56</sup> R	ND	R R ND	R	R R	No data	R R <sup>30</sup>	R R R	R R R
R R <sup>10</sup>	R R	R R	R R ND	R R	R	No data	R R <sup>30</sup>	R R R	R R R
R R	R R	No data	R R ND	R	R R	R R R	R R	R R R	R R <sup>30</sup>
R R	R R	R R R	R R R	R R	R R	R R R	R R	R R R	R R R <sup>30</sup>
R R	R R	R R R	R R R	R R	R R	R R R	R R	R R R	R R R <sup>30</sup>
R R	R R	R R R	R R R	R R	R R	R R R	R R	R R R	R R R <sup>30</sup>
R R	R R	R R R	R R R	R R	R R	R R R	R R	R R R	R R R <sup>30</sup>
R ND	R R	ND	R R ND	No data	R R	No data	R R	No data	No data
R R	R R	R R	R R ND	R R	R	R R R	R ND	R ND ND	R R <sup>30</sup> R <sup>65</sup>

RUBBERS																																		
	Butyl Rubber and Halo-Butyl Rubber			Ethylene Propylene Rubber (q)			Hard Rubber (Ebonite) (h)			Soft Natural Rubber (l)			Neoprene (i)			Nitrile Rubber			Chlorosulphonated Polyethylene			Polyurethane Rubber (v)			Silicone Rubbers (k)									
	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°							
Acetaldehyde	R	R	ND	R	R	ND	R	R	R	R <sup>80</sup>	R <sup>80</sup>	ND	R	R	R <sup>14</sup>	R	R	R	R	R	ND	ND	R	R	R	R	R	R						
Acetic acid (10%)	R <sup>14</sup>	R	R	R	R <sup>14</sup>	ND	R	R	R	R	R	R	R	R	R <sup>14</sup>	R	R	R	R	ND	R <sup>80</sup>	R <sup>80</sup>	R	R	R	R	R	R						
Acetic acid (glac. & anh.)	R <sup>14</sup>	R	R	R <sup>14</sup>	R <sup>14</sup>	ND	R	R	R <sup>14</sup>	R	R	R	R <sup>95</sup>	R	R <sup>14</sup>	R	R	R	R	ND	R <sup>80</sup>	R <sup>80</sup>	R	R	R	R	R	R						
Acetic anhydride	R <sup>80</sup>	R	R	No data	R	R <sup>30</sup>	R	R	R	R	R	R	R	R	ND	R	R	R	R	ND	R	R	R	R	R	R	R	R	R					
Acetone	R	R	R	R <sup>60</sup>	R <sup>60</sup>	R	R	R	R	R	R	R <sup>60</sup>	R	ND	R	R	R	R	ND	R <sup>15</sup>	ND	ND	R	R	R	R	R	R	R	R	R			
Other ketones	R <sup>13</sup>	R	R	R <sup>60</sup>	R <sup>60</sup>	R	R	R	R <sup>13</sup>	R	R	R <sup>30</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R				
Acetylene	R	R <sup>80</sup>		No data	R	R	R	R	R	R	R	R	R	R	R	ND	ND	R	R	R	R <sup>14</sup>	R	R	ND	ND		No data	R	R	R				
Acid fumes	R <sup>2</sup>	R	R	R <sup>2</sup>	R <sup>2</sup>	R <sup>2</sup>	R	R	R	R	R	R	R <sup>2</sup>	R	R <sup>2,80</sup>	R	R	R	R <sup>2</sup>	R	R	R	R	R <sup>2</sup>	R <sup>2</sup>	R <sup>2</sup>	R	R <sup>2</sup>	R	R				
Alcohols (most fatty)	R	R		R <sup>60</sup>	R <sup>60</sup>	R	R	R	R <sup>30</sup>	R	R	R <sup>60</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>30</sup>			
Aliphatic esters																															R <sup>30</sup>	R	R	
Alkyl chlorides																															R <sup>21</sup>	R	R	
Alum	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Aluminium chloride	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>4</sup>	
Ammonia, anhydrous	R	R	ND	R	R	ND	R	R	R	R	R	R	R <sup>80</sup>	R	R	R	R	R	R	R	R <sup>10</sup>	ND	ND	R <sup>80</sup>	R	R	R	R	R	R	R	R	R	
Ammonia, aqueous	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>80</sup>	R	R	R	R	R	R	R	R	R	R <sup>30</sup>	R <sup>80</sup>	R	R	R	R	R	R	R	
Ammonium chloride	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Amyl acetate	R <sup>80</sup>																														R <sup>21</sup>	R	R	
Aniline	R	R	ND																												R	R	R	
Antimony trichloride	R	R	R	No data	R	R	R	R	R	R	R	R	R	No data	No data	R	R	R	R	R	R	R	R	R	ND	ND	R	R	R	R	R	R	R	
Aqua regia																															R	R	R	
Aromatic solvents																R <sup>62</sup>	R													R <sup>21</sup>	R	R		
Beer	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>86</sup>	R	R	R	R	R	R	R	R	R	R	R	
Benzoic acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	No data	R	R	R	R	R	R	R	R	R	R	R	
Boric acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Brines, saturated	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Bromine				No data																														
Calcium chloride	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Carbon disulphide																						R	ND	ND	R	R	R	R	R	R	R	R	R	
Carbonic acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Carbon tetrachloride																																		
Caustic soda & potash	R	R	R	R	R	R	R	R	R <sup>13</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>30</sup>	R <sup>30</sup>	R	R	R	R	R	R	R <sup>30</sup>	
Chlorates of Na, K, Ba	R	R	R	R	R	R	R	R	R	R	R	R	No data	No data	R	R	R	R	R	R	No data	R	R	R	R	R	R	R	R	R	R	R		
Chlorine, dry	R <sup>50</sup>	R	R	R <sup>50</sup>	R <sup>50</sup>	R <sup>50</sup>	R <sup>30</sup>	R	R	R	R	R										No data	R	R	R	R	R	R	R	R	R	R		
Chlorine, wet	R <sup>80</sup>	R	R	R <sup>30</sup>	R <sup>30</sup>	R <sup>30</sup>	R <sup>13</sup>	R	R	R	R	R										R <sup>3</sup>	ND	ND	R	R	R	R	R	R	R	R	R	
Chlorides of Na, K, Mg	R	R	R	R	R	R	R	R	R	R	R	R <sup>80</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Chloroacetic acids	R <sup>10</sup>						R <sup>2</sup>	R	R																									
Chlorobenzene																																		
Chloroform																																		
Chlorosulphonic acid	R <sup>13</sup>	R <sup>13</sup>		R <sup>13</sup>	R <sup>13</sup>		R <sup>13</sup>	R	ND													No data	R <sup>30</sup>	ND	R <sup>30</sup>	ND		No data	R	R	R			
Chromic acid (80%)																						R <sup>30</sup>	R	ND	R	R	R	R	R	R	R	R	R	
Citric acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Copper salts (most)	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Cresylic acids (50%)	R <sup>4</sup>			No data																														
Cyclohexane																																		
Detergents, synthetic	R <sup>13</sup>	R	R	R <sup>13</sup>	R <sup>13</sup>	R <sup>13</sup>	R	R	R	R <sup>80</sup>	R <sup>80</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>30</sup>	R <sup>30</sup>	R	R	R	R	R	R	R	
Emulsifiers (all conc.)	R	R	R	No data	R	R <sup>4</sup>	R <sup>4</sup>			No data			R <sup>30</sup>	R	R	R	R	R	R	R	R	R <sup>30</sup>	R	R	R	R	R	R	R	R	R	R	R	
Ether																																		
Fatty acids (>C <sub>6</sub> )	R <sup>1</sup>	R <sup>80</sup>	R	R <sup>80</sup>	R <sup>80</sup>		R <sup>80</sup>	R <sup>13</sup>	R <sup>30</sup>				R	R	R	R	R <sup>4</sup>	R	R	R	R	R	R	R <sup>4</sup>	R <sup>80</sup>	R	R	R	R	R	R	R		
Ferric chloride	R	R	R	R	R	R	R	R	R	R <sup>80</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Ferrous sulphate	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	
Fluorinated refrigerants, aerosols, e.g. Freon	R <sup>4</sup>	ND	ND	No data			No data			No data			R <sup>30</sup>	R	ND	R <sup>30</sup>	R	R	R <sup>30</sup>	R	R	R <sup>30</sup>	ND	ND	ND	ND	R	R	R	R <sup>4,21</sup>				
Fluorine, dry	R <sup>80</sup>	ND	ND	R <sup>80</sup>	ND	ND	R <sup>13</sup>	R <sup>13</sup>	ND													No data	R <sup>13</sup>	R <sup>13</sup>	R	R	R	R	R	R	R	R	R	
Fluorine, wet	R <sup>80</sup>	ND	ND	R <sup>80</sup>	ND	ND	R <sup>13</sup>	R <sup>13</sup>	ND													No data	R	R	R	R	R	R	R	R	R	R		
Fluosilicic acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R							No data	R	R	R	R	R	R	R	R	R	R	R	R
Formaldehyde (40%)	R <sup>80</sup>			R <sup>80</sup>			R	R <sup>30</sup>	R	R <sup>14</sup>			R	ND	ND	R			R			R			ND	ND	R	R	R	R	R	R		
Formic acid	R <sup>13</sup>	R	R	R <sup>14</sup>	R <sup>14</sup>		R	R <sup>80</sup>		R <sup>80</sup>			R	R	R	R			R			R			R	R	R	R	ND	ND	R	R	R	

MISCELLANEOUS					
Concrete (s)	Glass (t)	Graphite (u)	Porcelain and Stoneware	Vitreous Enamel (w)	Wood (z)
20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°
No data	No data	R R R	R R R	R R R	R R R
	R R R	R R R	R R R	R R R	R R
	R R R	R R R	R R R	R R R	
	No data	R R R	R R R	R ND ND	
R R R	R R R	R R R	R R R	R R R	R R R
R R R	No data	R R R	R R R	R R R	R R R
	R R R	R R R	R R R	R R R	
R R R	R <sup>5</sup> R R	R R R	R R R	R <sup>5</sup> R ND	No data
R R R	R R R	R R R	R R R	R R R	R R
	R R R	R R R	R R R	R R R	R R R
	R R R	R R R	R R R	R R ND	
	R R R	R R R	R R R	R R R	R R
	R <sup>30</sup>	R R R	R R R	R R ND	
No data	No data	R R R	R R R	R R R	
R R R	R R R <sup>50</sup>	R R R	R R R	R ND	
	R R R	R R R	R R R	R ND	R R
	R R R	R R R	R R R	R R R	R R R
No data	R R R	R R R	R R R	R R R	R R
No data	R R R	R R R	R R R	R R R	
R R R	R R R	R R R	R R R	R R ND	R R R
R R R <sup>35</sup>	R R R	R R R	R R R	R R R	R R R
No data	R R R	R R R	R R R	R R ND	R R R
R R R	R R R	R R R	R R R	R R ND	R R R
R R R	R R R	R R R	R R R	R R ND	R
	R R R	R R R	R R R	No data	
R <sup>44</sup> R R	R ND ND	R R R	R R R	R ND	R R
R R R	R ND ND	R R R	R R R	R R R	
R <sup>50</sup> R R	R R R	R R R	R R R	R R R	R R R
R R R	R R R	R R R	R R R	R R R	R R R
R <sup>72</sup> R R	ND	R <sup>13</sup> R R	R <sup>10</sup>	R <sup>10</sup>	
R R R	R R R	R R R	R R R	No data	R ND ND
No data	No data	R R R	R R R	R R R	
	ND	R R R	R R R	No data	
R <sup>12</sup> R R	R R R	R R R	R R R	R R	R R
	R R R	R R R	R R R	R ND ND	
R R R	R R R	R R R	R R R	R R R	R R
R R R	R R R	R R R	R R R	R R R	R R R
	No data	R R R	R R R	No data	
	R R ND	R R R	R R R	R ND ND	
	R R ND	R R R	R R R	R R R	R R
R <sup>51</sup> R R	R R R	R R R	R R R	R R R	R R R
	No data	R R R	R R R	R R ND	
R R R	No data	R R R	R R R	R R R	R R R
R <sup>81</sup> R R	R <sup>13</sup> R <sup>30</sup>	R R R	R R R	R R R	R R R
No data	R R R	R R R	R R R	R R R	R R
R R R	R R R	R R R	R R R	R R R	R
	R R R	R R R	R R R	R R R	R R
	R R R	R <sup>13</sup> R R	R R R	R ND	R <sup>14</sup>
	R R R	R R R	R R R	R ND	R <sup>14</sup>
R R R	No data	R R R	R <sup>39</sup> R R	No data	R R R
No data		R R R		R ND	No data
No data		R R R		No data	No data
R R R		R R R			No data
R <sup>80</sup>	R R R	R R R	R R R	R R R	R R
	R R R	R R R	R R R	R R R	

NOTES

Explanatory notes at lower temperatures may be taken to apply also at higher temperatures unless otherwise shown.

- 1 Not anhydrous
- 2 Depending on the acid
- 3 35%
- 4 Fair resistance
- 5 Not HF fumes
- 6 Up to 40%
- 7 Saturated solution
- 8 Pineapple and grapefruit juices 20°C
- 9 Photographic emulsions up to 20°C
- 10 10%
- 11 Anhydrous
- 12 Not Mg
- 13 Depending on concentration
- 14 Discoloration and/or swelling and softening
- 15 Up to 25%
- 16 Not chloride/not if chloride ions present
- 17 Not fluorinated silicone rubbers
- 18 Up to 60%
- 19 Up to 50%
- 20 Not aerated solutions
- 21 Fluorinated silicone rubbers only
- 22 ND for Mg
- 23 5%
- 24 Pure only
- 25 Up to 30%
- 26 If no iron salts or free chlorine
- 27 May crack under stressed conditions
- 28 45%
- 29 55%
- 30 Depending upon composition
- 31 Chloride
- 32 20%
- 33 Depending on alcohol
- 34 Data for sodium
- 35 Fresh
- 36 Over 85%
- 37 Some attack at high temperature
- 38 Neutral
- 39 Attacked by fluoride ions
- 40 Sulphate and nitrate
- 41 Softening point
- 42 In strong solutions only when inhibited
- 43 Depending on water conditions
- 44 Dilute
- 45 Up to 15%
- 46 Not methyl
- 47 Drawn wire
- 48 Some attack, but protective coating forms
- 49 Using anodic passivation techniques
- 50 Some attack/absorption/slow erosion
- 51 Not sulphate
- 52 70%
- 53 In absence of dissolved O<sub>2</sub> and CO<sub>2</sub>
- 54 75%
- 55 80%
- 56 May cause stress cracking
- 57 Pitting possible in stagnant solutions
- 58 In presence of H<sub>2</sub>SO<sub>4</sub>
- 59 Not ethyl
- 60 May discolour liquid
- 61 The material can cause decomposition
- 62 Depending on type
- 63 95%
- 64 Slight plating will occur
- 65 Not recommended under certain conditions of temperature, etc.
- 66 65%
- 67 Aerated solution
- 68 Estimated effect
- 69 Up to 90%
- 70 Not oxidising conditions
- 71 Not lower members of series
- 72 Not high alumina cement concrete

RUBBERS																															
	Butyl Rubber and Halo-Butyl Rubber			Ethylene Propylene Rubber (q)			Hard Rubber (Ebonite) (h)			Soft Natural Rubber (h)			Neoprene (i)			Nitrile Rubber			Chlorosulphonated Polyethylene			Polyurethane Rubber (v)			Silicone Rubbers (k)						
	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°				
Fruit juices	R <sup>80</sup>	R <sup>80</sup>		R <sup>60</sup>	R <sup>60</sup>		R <sup>65</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R				
Gelatine	R	R	R	R	R		R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R				
Glycerine	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R				
Glycols	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R				
Hexamine	R	R	ND		No data		R	R	ND		R	R	ND		R <sup>37</sup>	R		No data		R	R	R	ND	ND		No data					
Hydrazine	R	R	ND	R	ND	ND	R							R <sup>44</sup>	ND	ND	R		No data		ND	ND				No data					
Hydrobromic acid (50%)	R	R	R	R	R	ND	R	R <sup>27</sup>	R <sup>27</sup>	R <sup>65</sup>	R		R	ND	ND	R			R	R	ND	R <sup>15</sup>	R <sup>15</sup>	R <sup>80</sup>		R	R	R			
Hydrochloric acid (10%)	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		R	R		R	R				R	R	R		
Hydrochloric acid (conc.)	R <sup>4</sup>	R	R	R	R <sup>4</sup>	R <sup>80</sup>	R	R <sup>27</sup>	R <sup>27</sup>	R	R <sup>80</sup>		R	R <sup>95</sup>	ND				R	R		R	R				R <sup>30</sup>				
Hydrocyanic acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R			R		R	R	ND	R	R		No data				
Hydrofluoric acid (40%)	R <sup>30</sup>	R	R	R <sup>30</sup>	R <sup>30</sup>	ND	R <sup>30</sup>	R	R	R <sup>30</sup>	R <sup>30</sup>		R	ND	ND				R	R	ND	R	R								
Hydrofluoric acid (75%)				R <sup>30</sup>	ND	ND													R	R	ND										
Hydrogen peroxide (30%)	R <sup>80</sup>	R	R	R <sup>80</sup>	ND	ND	R <sup>80</sup>							R	R		R			R <sup>87</sup>	R <sup>87</sup>		R <sup>4</sup>	ND		R	R	R			
(30-90%)	R <sup>80</sup>	R <sup>87</sup>	ND				R <sup>87</sup>							R	R				R <sup>87</sup>	R <sup>87</sup>						R <sup>30</sup>	R	R			
Hydrogen sulphide	R	R	R	R	R	R	R	R	R	R	R	R	R	R	ND				R	ND	ND	R	R			No data					
Hypochlorites	R <sup>30</sup>	R <sup>80</sup>		R	R	ND	R <sup>13</sup>	R		R <sup>80,76</sup>	R <sup>13</sup>		R	R		R			R	R	R	R	R		R <sup>30</sup>	ND	R	R	R		
Lactic acid (100%)	R	R	ND	R	R	ND	R	R	R	R	R <sup>14,80</sup>		R	R	R	R	R		R	R	R	R	R		R <sup>23</sup>	R <sup>23</sup>	R	R	R		
Lead acetate	R	R	R	R	R	R	R	R	R	R <sup>80</sup>	R	R	R	R	R	R	ND	ND		No data		R	R		R	R	R	R	R		
Lime (CaO)	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	ND		No data	R	R		R	R	R	R	R		
Maleic acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	ND					No data	R	R		R	R	R	R	R		
Meat juices	R	R	R	R	R	R	R <sup>13</sup>	R	R	R <sup>13</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Mercuric chloride	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Mercury	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Milk & its products	R <sup>80</sup>	R	R	R <sup>80</sup>	R <sup>80</sup>		R	R	R				R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Moist air	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Molasses	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	ND	ND		R <sup>86</sup>	R	R		R	R	R	R	R	R		
Naphtha																			R	R		R <sup>38</sup>					R <sup>21</sup>	R	R		
Naphthalene																											R <sup>21</sup>	R	R		
Nickel salts	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Nitrates of Na, K, NH <sub>3</sub>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Nitric acid (<25%)	R <sup>23</sup>	R <sup>23</sup>	R <sup>23</sup>				R <sup>101</sup>	R		R <sup>101</sup>			R	R	R	R						R	R				R	R	R		
Nitric acid (50%)																															
Nitric acid (95%)																															
Nitric acid, fuming																															
Oils, essential	R <sup>14</sup>	R	ND	R <sup>60</sup>	ND	ND	R <sup>14</sup>			No data			R <sup>14</sup>	ND	ND	R <sup>4</sup>	R <sup>4</sup>								R	R	R <sup>30</sup>	R	R		
Oils, mineral				R <sup>80</sup>	R <sup>80</sup>	R <sup>80</sup>							R	ND	ND	R	R	R				R <sup>30</sup>			R	R	R <sup>30</sup>	R	R		
Oils, vegetable & animal	R	R <sup>14</sup>		R <sup>14</sup>	R <sup>14</sup>		R <sup>80</sup>	R	R	R <sup>14</sup>	R		R <sup>14</sup>	ND	ND	R	R	R				R <sup>30</sup>			R	R	R	R	R		
Oxalic acid	R	R	R		No data		R	R	R	R <sup>80</sup>	R	R	R	R	R	R	R					R	ND	ND		ND	ND	R	R	R	
Ozone	R	R		R	R		R	R	R				R	R	R	R	R	R				R <sup>30</sup>			R	R	R	R	R		
Paraffin wax	R	R	R	R	R	ND	R	R	R	R	R <sup>14</sup>		R	R	R	R	R	R				R	R	R	R	R	R	R	R		
Perchloric acid	R			R																		No data		ND	ND		No data				
Phenol	R	R <sup>80</sup>	ND	R <sup>80</sup>			R <sup>13</sup>	R																				R	R	R	
Phosphoric acid (25%)	R	R	R	R	R	R	R	R	R <sup>60</sup>	R	R	R <sup>60</sup>	R	R	R	R	R	ND				R	R	R	R	R	R	R	R		
Phosphoric acid (50%)	R	R	R	R	R	R	R	R	R <sup>60</sup>	R	R	R <sup>60</sup>	R	R	R	R	R					R	R	R	R	R	R	R	R		
Phosphoric acid (95%)	R	R	R	R	R	R	R <sup>36</sup>	R	R <sup>60</sup>	R <sup>36</sup>	R	R <sup>60</sup>	R	R	R	R						R	R	R		R <sup>30</sup>	R	R	R		
Phosphorus chlorides	R				No data			No data			No data			No data																	
Phosphorus pentoxide	R	R	ND	R	R	ND	R	R		R	R		R	R	R							No data		ND	ND		R	R	R		
Phthalic acid	R <sup>13</sup>	R	R	R <sup>13</sup>	R <sup>13</sup>	ND	R <sup>80</sup>	R <sup>80</sup>	R <sup>80</sup>	R <sup>80</sup>			R	R	R	R	ND	ND			No data	R	ND	ND		R	R	R	R		
Picric acid	R <sup>80</sup>	R	R		No data		R	R <sup>30</sup>	R	R	R <sup>30</sup>		R	R	R							R <sup>13</sup>		R	R		ND	ND		No data	
Pyridine	R <sup>4</sup>																														
Sea water	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Silicic acid	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	ND															
Silicone fluids	R	R	ND		No data		R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	ND	R	R	R	
Silver nitrate	R	R	R	R <sup>60</sup>	R <sup>60</sup>	R <sup>60</sup>	R <sup>61</sup>			R <sup>80</sup>	R		R	R	R	R	ND					R	R	R	R	R	R	R	R		
Sodium carbonate	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R		
Sodium peroxide	R	R	R	R	R	ND	R <sup>13</sup>	R		R <sup>80</sup>	R <sup>80</sup>	ND		R	R <sup>97</sup>	ND						R <sup>13</sup>		R	R		ND	ND			

MISCELLANEOUS																	
Concrete (s)			Glass (t)			Graphite (t)			Porcelain and Stoneware			Vitreous Enamel (w)			Wood (z)		
20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°	20°	60°	100°
R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
No data			R	ND	ND	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	R	R	R	No data		
			R	R	R <sup>50</sup>	R	R	R	R	R	R	No data					
			R	R	R <sup>50</sup>	R	R	R	R	R	R	R	R	R	R		
			R	R	R <sup>50</sup>	R	R	R	R	R	R	R	R	ND	R		
			R	R		R	R	R	R	R	R	R	ND	ND	R	R	
						R	R	R									
						R	R	R									
No data			R	R	R	R	R	R	R	R	R	R	R	R			
No data			R	R	R	R	R	R	R	R	R	R	R	R			
						R	R	R	R	R	R	R	R	R	R	R	R
R <sup>72</sup>	R	R	R	R	R	R	R <sup>37</sup>	R <sup>37</sup>	R	R	R	R	R	ND			
			No data			R	R	R	R	R	R	R	R	R	R		
No data			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	R	R	R	R	R	R	R	R	R	R	ND	R <sup>14</sup>	R	R	R
No data			No data			R	R	R	R	R	R	R	R	R	R	R	R
No data			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	No data			R	R	R
R	R	R	R	R	R	R	R	R	R	R	R	R	ND	R	R	R	R
R <sup>35</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R <sup>14</sup>	R <sup>14</sup>	R <sup>14</sup>
R			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	No data			R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	No data			R	R	R	R	R	R	R	R	R	R	R	R
No data			R	R	R	R	R	R	R	R	R	No data			R	R	R
R <sup>73</sup>	R	R	R	ND	ND	R	R	R	R	R	R	R	ND	ND	R	R	R
			R	R	R <sup>50</sup>	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R <sup>50</sup>				R	R	R	R	R	ND			
			R	R	R <sup>50</sup>				R	R	R	R	ND	ND			
			R	R	R <sup>50</sup>				R	R	R	R	ND	ND			
No data			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	R	R	R	R	R	R	R	R	R	No data			No data		
R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R <sup>15</sup>	R <sup>10</sup>		R	R	R	No data					
			R	ND	ND	R	R	R	R	R	R	R	R	R			
			R	R	R	R	R	R	R	R	R	R	R	R			
			R	R	R	R	R	R	R	R	R	R	R	R			
			R	R	R	R	R	R	R	R	R	R	R	ND			
			R	R	R	R	R	R	R	R	R	R	R	ND			
			R	ND	ND	R	R	R	R	R	R	No data					
			R	R	R	R	R	R	R	R	R	No data					
			R	R	R	R	R	R	R	R	R	R	R	R	R	R	
			R	R	R	R	R	R	R	R	R	R	R	R	No data		
No data			R	R	R	R	R	R	R	R	R	R	R	R	R <sup>14</sup>		
R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R	R	R	R	R	ND	R	R	R	R	R	R	R	ND	R	R	R	R
R <sup>74</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
No data			R	R	R	R	R	R	R	R	R	R	R	R	R	R	R
R <sup>72</sup>	R	R	R	R	R	R	R	R	R	R	R	R	R	R			
R <sup>72</sup>	R	R	R	ND	ND	No data			R	R	R	No data					

- 73 Not ammonium
- 74 Not chlorosilanes
- 75 Data for ammonium
- 76 Data for calcium
- 77 Data for potassium
- 78 In presence of heavy metal ions
- 79 ND for Ba
- 80 Limited service
- 81 Except those containing sulphate
- 82 Provided less than 70% copper
- 83 Water less than 150 ppm
- 84 May cause some localised pitting
- 85 60% in one month
- 86 Low taste and odour
- 87 Catalyses decomp. of H<sub>2</sub>O<sub>2</sub>
- 88 65%
- 89 1–2 days
- 90 Wet gas
- 91 Less than 0–005% water
- 92 In absence of heavy metal ions oxidising agents
- 93 Stress corrosion in MeOH and halides (not in other alcohols)
- 94 When free of SO<sub>2</sub>
- 95 50% swell in 28 days
- 96 60% swell in 3 days
- 97 Could be dangerous in black loaded compounds
- 98 Not alkaline
- 99 Ozone 2% Oxygen 98%
- 100 This is the softening point
- 101 Nitric acid less than 5% concentration
- 102 Acid fumes dry. Attack might occur if moisture present and concentrated condensate built up
- 103 Stainless steels not normally recommended for caustic applications
- 104 In the absence of impurities
- 105 10% w/w in alcohol
- 106 Swelling with some ketones
- 107 Some stress cracking at high pH
- (a) **Aluminium:** In many cases where the chart indicates that aluminium is a suitable material there is some attack, but the corrosion is slight enough to allow aluminium to be used economically.
- (b) **Brass:** Some types of brass have less corrosion resistance than is shown on the chart, others have more, e.g. Al brass.
- (c) **Cast iron:** This is considered to be resistant if the material corrodes at a rate of less than 0.25 mm per annum. When choosing cast iron, Ni-Resist or high Si iron for a particular application the very different physical properties of these materials must be taken into account.
- (d) **Gunmetal:** The data refer only to high tin gunmetals.
- (e) **Nickel-copper alloys:** The physical properties are for annealed material. Both the tensile strength and hardness can vary with form and heat treatment condition.
- (f) **Stainless steels:** Less expensive 13% chromium steels may be used for some applications instead of 18/8 steels. Under certain conditions the addition of titanium increases the corrosion resistance of 18/8 steels. Also, it produces materials which can be welded without the need for subsequent heat treatment. These steels are, however, inferior in corrosion resistance to the more expensive 18/8/Mo steels.
- (g) **Tin:** Data refer to pure or lightly alloyed tin; not to discontinuous tin coatings.
- (h) **Soft natural rubber and ebonite:** Performance at higher temperatures depends on method of compounding.
- (i) **Neoprene:** Brush or spray applied 1.5 mm thick, and properly cured.
- (k) **Silicone rubbers:** Withstand temperatures ranging from –90°C to above 250°C and are resistant to many oils and chemicals. In some cases particularly good resistance is shown by the fluorinated type.

RUBBERS										
	Butyl Rubber and Halo-Butyl Rubber	Ethylene Propylene Rubber (q)	Hard Rubber (Ebonite) (h)	Soft Natural Rubber (h)	Neoprene (i)	Nitrile Rubber	Chlorosulphonated Polyethylene	Polyurethane Rubber (v)	Silicone Rubbers (k)	
	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	20° 60° 100°	
Sodium silicate	R R R	R R R	R R R	R R R	R R R	R R ND	R R R	R R	R R R	
Sodium sulphide	R R R	R R R	R R R	R R R	R R R	R R ND	No data	R ND	R R R	
Stannic chloride	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	
Starch	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	
Sugar, syrups, jams	R <sup>13</sup> R R	R <sup>60</sup> R <sup>60</sup> R <sup>60</sup>	R <sup>13</sup> R R	R <sup>13</sup> R R	R R R	R R R	R R R	R R	R R R	
Sulphamic acid	No data	R R ND	R <sup>13</sup> R	No data	R ND ND	No data	R R R	R R	No data	
Sulphates (Na, K, Mg, Ca)	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	
Sulphites	R R R	R R R	R R R	R <sup>80</sup> R <sup>80</sup>	R R R	R R R	R R R	R R	R R R	
Sulphonic acids	R <sup>13</sup> R	R <sup>13</sup> R <sup>13</sup> R <sup>13</sup>	R <sup>2</sup> R <sup>2</sup> R <sup>2</sup>	R R R	R R R	ND	R R R	R ND	No data	
Sulphur	R R R	R R R	R R R	R	R R R	R <sup>30</sup> R R	R R R	ND ND	R R R	
Sulphur dioxide, dry	R R R	R R R	R R R		R R R			ND ND	R R ND	
Sulphur dioxide, wet	R R R	R R R	R R R <sup>4</sup>		R R R		R <sup>4</sup> R R	ND ND	R R ND	
Sulphur trioxide						No data			R R R	
Sulphuric acid (<50%)	R R R	R R R	R R R	R R	R R R	R	R R R	R <sup>25</sup> R <sup>25</sup> <sub>80</sub>	R R R	
Sulphuric acid (70%)		R <sup>80</sup>	R <sup>66</sup>		R		R R		No data	
Sulphuric acid (95%)							R			
Sulphuric acid, fuming										
Sulphur chlorides						No data	No data			
Tallow	R R R <sup>4</sup>	R R <sup>4</sup> ND	R R R	R R	R R R	R R R	R R R	R ND	R <sup>30</sup> R R	
Tannic acid (10%)	R R R	R R R	R R R	R R R	R R R	R R	R R R	R R	R R R	
Tartaric acid	R R R	R R R	R R R	R R R	R R R	R R	R R R	R R	R R R	
Trichlorethylene						R <sup>65</sup>			R <sup>21</sup> R R	
Vinegar	R R R	R R <sup>14</sup>	R R R	R <sup>80</sup> R	R R R	R R <sup>37</sup> R	R R R	R <sup>80</sup> R <sup>80</sup>	R R R	
Water, distilled	R R R	R R R	R <sup>30</sup> R R	R <sup>30</sup> R R	R R R	R R R	R R R	R R	R R R	
Water, soft	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	
Water, hard	R R R	R R R	R R R	R R R	R R R	R R R	R R R	R R	R R R	
Yeast	R R R	No data	R R R	R R R	R R R	R ND ND	R R R	ND ND	R R R	
Zinc chloride	R R R	R R R	R R R	R R R	R R R	R R ND	R R R	R R	R R R	







## APPENDIX C

# *Physical Property Data Bank*

Inorganic compounds are listed in alphabetical order of the principal element in the empirical formula.

Organic compounds with the same number of carbon atoms are grouped together, and arranged in order of the number of hydrogen atoms, with other atoms in alphabetical order.

NO	= Number in list
MOLWT	= Molecular weight
TFP	= Normal freezing point, deg C
TBP	= Normal boiling point, deg C
TC	= Critical temperature, deg K
PC	= Critical pressure, bar
VC	= Critical volume, cubic metre/mol
LDEN	= Liquid density, kg/cubic metre
TDEN	= Reference temperature for liquid density, deg C
HVAP	= Heat of vaporisation at normal boiling point, J/mol
VISA, VISB	= Constants in the liquid viscosity equation:

$\text{LOG}[\text{viscosity}] = [\text{VISA}] * [(1/T) - (1/\text{VISB})]$ , viscosity mNs/sq.m, T deg K.

DELHF = Standard enthalpy of formation of vapour at 298 K, kJ/mol.

DELGF = Standard Gibbs energy of formation of vapour at 298 K, kJ/mol.

CPVAPA, CPVAPB, CPVAPC, CPVAPD = Constants in the ideal gas heat capacity equation:

$C_p = \text{CPVAPA} + (\text{CPVAPB}) * T + (\text{CPVAPC}) * T ** 2 + (\text{CPVAPD}) * T ** 3$ ,

$C_p$  J/mol K, T deg K.

ANTA, ANTB, ANTC = Constants in the Antoine equation:

$\text{Ln}(\text{vapour pressure}) = \text{ANTA} - \text{ANTB}/(T + \text{ANTC})$ , vap. press. mmHg, T deg K.

To convert mmHg to N/sq.m multiply by 133.32.

To convert degrees Celsius to Kelvin add 273.15.

TMN = Minimum temperature for Antoine constant, deg C

TMX = Maximum temperature for Antoine constant, deg C

Most of the values in this data bank were taken, with the permission of the publishers, from: The Properties of Gases and Liquids, by Reid, R. C., Sherwood, T. K. and Prausnitz, J. M., 3rd edn, McGraw-Hill.

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
1	AR	ARGON	39.948	-189.9	-185.9	150.8	48.7	0.075	1373	-183	6531	1
2	BCL3	BORON TRICHLORIDE	117.169	-107.3	12.5	452.0	38.7		1350	11		2
3	BF3	BORON TRIFLUORIDE	67.805	-126.7	-99.9	260.8	49.9					3
4	BR2	BROMINE	159.808	-7.2	58.7	584.0	103.4	0.127	3119	20	30,187	4
5	CLNO	NITROSYL CHLORIDE	65.459	-59.7	-5.5	440.0	91.2	0.139	1420	-12	25,707	5
6	CL2	CHLORINE	70.906	-101.0	-34.5	417.0	77.0	0.124	1563	-34	20,432	6
7	CL3P	PHOSPHORUS TRICHLORIDE	137.333	-112.2	75.8	563.0		0.260	1574	21		7
8	CL4SI	SILICON TETRACHLORIDE	169.898	-68.9	57.2	507.0	37.5	0.326	1480	20	27,549	8
9	D2	DEUTERIUM	4.032	-254.5	-249.5	38.4	16.6	0.060	165	-250	1223	9
10	D2O	DEUTERIUM OXIDE	20.031	3.8	101.4	644.0	216.6	0.056	1105	20	41,366	10
11	F2	FLUORINE	37.997	-219.7	-188.2	144.3	52.2	0.066	1510	-188	6531	11
12	F3N	NITROGEN TRIFLUORIDE	71.002	-206.8	-129.1	234.0	45.3		1537	-129		12
13	F4SI	SILICON TETRAFLUORIDE	104.080	-90.2	-86.2	259.0	37.2		1660	-95		13
14	F6S	SULPHUR HEXAFLUORIDE	146.050	-50.7	-63.9	318.7	37.6	0.198	1830	-50		14
15	HBR	HYDROGEN BROMIDE	80.912	-86.1	-67.1	363.2	85.5	0.100	2160	-57	17,668	15
16	HCL	HYDROGEN CHLORIDE	36.461	-114.2	-85.1	324.6	83.1	0.081	1193	-85	16,161	16
17	HF	HYDROGEN FLUORIDE	20.006	-83.2	19.5	461.0	64.8	0.069	967	20	6699	17
18	HI	HYDROGEN IODIDE	127.912	-50.8	-35.6	424.0	83.1	0.131	2803	-36	19,778	18
19	H2	HYDROGEN	2.016	-259.2	-252.8	33.2	13.0	0.065	71	-253	904	19
20	H2O	WATER	18.015	0.0	100.0	647.3	220.5	0.056	998	20	40,683	20
21	H2S	HYDROGEN SULPHIDE	34.080	-85.6	-60.4	373.2	89.4	0.099	993	-60	18,673	21
22	H3N	AMMONIA	17.031	-77.8	-33.5	405.6	112.8	0.073	639	0	23,362	22
23	H3P	PHOSPHINE	33.998	-133.8	-87.5	324.8	62.7	0.113			14,725	23
24	H4N2	HYDRAZINE	32.045	1.5	113.5	653.0	146.9	0.096	1008	20	44,799	24
25	H4SI	SILANE	32.112	-185.0	-112.2	269.7	48.4		680	88		25
26	HE(4)	HELIUM-4	4.003	-269.0		5.2	2.3	0.057	123	-269	92	26
27	I2	IODINE	253.808	113.6	184.3	819.0	116.5	0.155	3740	180	41,868	27
28	KR	KRYPTON	83.800	-157.4	-153.4	209.4	55.0	0.091	2420	-153	9667	28
29	NO	NITRIC OXIDE	30.006	-163.7	-151.8	180.0	64.8	0.058	1280	-152	13,816	29
30	NO2	NITROGEN DIOXIDE	46.006	-11.3	21.1	431.4	101.3	0.170	1447	20	19,071	30
31	N2	NITROGEN	28.013	-209.9	-195.8	126.2	33.9	0.090	805	-195	5581	31
32	N2O	NITROUS OXIDE	44.013	-90.9	-88.5	309.6	72.4	0.097	1226	-90	16,559	32
33	NE	NEON	20.183	-246.7	-246.2	44.4	27.6	0.042	1204	-246	1842	33
34	O2	OXYGEN	31.999	-218.8	-183.0	154.6	50.5	0.073	1149	-183	6824	34
35	O2S	SULPHUR DIOXIDE	64.063	-75.5	-10.2	430.8	78.8	0.122	1455	-10	24,932	35
36	O3	OZONE	47.998	-192.7	-111.9	261.0	55.7	0.089	1356	-112	11,179	36
37	O3S	SULPHUR TRIOXIDE	80.058	16.8	44.8	491.0	82.1	0.130	1780	45	40,679	37
38	XE	XENON	131.300	-111.9	-108.2	289.7	58.4	0.118	3060	-108	13,013	38
39	CBRF3	TRIFLUOROBROMOMETHANE	148.910		-59.2	340.2	39.7	0.200				39
40	CCLF3	CHLOROTRIFLUOROMETHANE	104.459	-181.2	-81.5	302.0	39.2	0.180			15,516	40
41	CCL2F2	DICHLORODIFLUOROMETHANE	120.914	-157.8	-29.8	385.0	41.2	0.217	1750	-115	19,979	41
42	CCL2O	PHOSGENE	98.916	-128.2	7.6	455.0	56.7	0.190	1361	20	24,409	42
43	CCL3F	TRICHLOROFLUOROMETHANE	137.368	-111.2	23.8	471.2	44.1	0.248			24,786	43
44	CCL4	CARBON TETRACHLORIDE	153.823	-23.2	76.5	556.4	45.6	0.276	1584	25	30,019	44
45	CF4	CARBON TETRAFLUORIDE	88.005	-186.8	-128.0	227.6	37.4	0.140			11,974	45
46	CO	CARBON MONOXIDE	28.010	-205.1	-191.5	132.9	35.0	0.093	803	-192	6046	46
47	COS	CARBONYL SULPHIDE	60.070	-138.9	-50.3	375.0	58.8	0.140	1274	-99		47
48	CO2	CARBON DIOXIDE	44.010	-56.6	-78.5	304.2	73.8	0.094	777	20	17,166	48
49	CS2	CARBON DISULPHIDE	76.131	-111.9	46.2	552.0	79.0	0.170	1293	0	26,754	49
50	CHBR3	BROMOFORM	94.940	-178.3	3.5	464.0	66.1	0.162	1733	0	24,241	50

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
1	107.57	58.76			20.804	-3.211E-05	51.665E-09		15.2330	700.51	-5.84	-192	-179	1
2														2
3														3
4	387.82	292.79			33.859	11.254E-03	-1.192E-05	45.343E-10	15.8441	2582.32	-51.56	-14	81	4
5			52.63	66.99	34.097	44.715E-03	-3.340E-05	10.149E-09	16.9505	2520.70	-23.46	-63	12	5
6	191.96	172.35			26.929	33.838E-03	-3.869E-05	15.470E-09	15.9610	1978.32	-27.01	-101	-9	6
7														7
8									15.8019	2634.16	-43.15	-35	91	8
9	19.67	8.38			30.250	-6.406E-03	11.698E-06	-3.684E-09	13.2954	157.89		-254	-248	9
10	757.92	304.58	-249.41	-234.80										10
11	84.20	52.52			23.216	36.568E-03	-3.462E-05	12.041E-09	15.6700	714.10	-6.00	-214	-182	11
12			-124.68	-127.19					15.6107	1155.69	-15.37	-170	-118	12
13														13
14	251.29	180.75	-1221.71	-1117.88					19.3785	2524.78	-11.16	-114	-53	14
15	88.08	166.32	-36.26	-53.30	30.647	-9.462E-03	17.224E-06	-6.238E-09	14.4687	1242.53	-47.86	-89	-52	15
16	372.78	277.74	-92.36	-95.33	30.291	-7.201E-03	12.460E-06	-3.898E-09	16.5040	1714.25	-14.45	-136	-73	16
17	438.74	199.62	-271.30	-273.40	29.061	66.110E-05	-2.032E-06	25.037E-10	17.6958	3404.49	15.06	-67	40	17
18	155.15	285.43	26.38	1.59	31.158	-1.428E-02	29.722E-06	-1.353E-08	12.9149	957.96	-85.06	-58	-17	18
19	13.82	5.39			27.143	92.738E-04	-1.381E-05	76.451E-10	13.6333	164.90	3.19	-259	-248	19
20	658.25	283.16	-242.00	-228.77	32.243	19.238E-04	10.555E-06	-3.596E-09	18.3036	3816.44	-46.13	11	168	20
21	342.79	165.54	-20.18	-33.08	31.941	14.365E-04	24.321E-06	-1.176E-08	16.1040	1768.69	-26.06	-83	-43	21
22	349.02	169.63	-45.72	-16.16	27.315	23.831E-03	17.074E-06	-1.185E-08	16.9481	2132.50	-32.98	-94	-12	22
23			229.44		23.228	44.003E-03	13.029E-06	-1.593E-08						23
24	524.98	290.88	95.25	158.64	9.768	18.945E-02	-1.657E-04	60.248E-09	17.9899	3877.65	-45.15	15	70	24
25			32.66	54.93	11.179	12.200E-02	-5.548E-05	68.412E-10	16.3424	1629.99	5.35	-111	-179	25
26									12.2514	33.73	1.79	-269	-269	26
27	559.62	520.55			35.592	65.147E-04	-6.988E-06	28.345E-10	16.1597	3709.23	-68.16	110	214	27
28									15.2677	958.75	-8.71	-160	-144	28
29			90.43	86.75	29.345	-9.378E-04	97.469E-07	-4.187E-09	20.1314	1572.52	-4.88	-178	-133	29
30	406.20	230.21	33.87	52.00	24.233	48.358E-03	-2.081E-05	29.308E-11	20.5324	4141.29	3.65	-43	47	30
31	90.30	46.14			31.150	-1.357E-02	26.796E-06	-1.168E-08	14.9542	588.72	-6.60	-219	-183	31
32			81.60	103.71	21.621	72.808E-03	-5.778E-05	18.301E-09	16.1271	1506.49	-25.99	-129	-73	32
33					20.786				14.0099	180.47	-2.61	-249	-244	33
34	85.68	51.50			28.106	-3.680E-06	17.459E-06	-1.065E-08	15.4075	734.55	-6.45	-210	-173	34
35	397.85	208.42	-297.05	-300.36	23.852	66.989E-03	-4.961E-05	13.281E-09	16.7680	2302.35	-35.97	-78	7	35
36	313.79	120.34	142.77	162.91	20.545	80.093E-03	-6.243E-05	16.973E-09	15.7427	1272.18	-22.16	-164	-99	36
37	1372.80	315.99	-395.53	-370.62	16.370	14.591E-02	-1.120E-04	32.423E-09	20.8403	3995.70	-36.66	17	59	37
38									15.2958	1303.92	-14.50	-115	-95	38
39			-649.37	-623.00										39
40			-695.01	-654.40	22.814	19.113E-02	-1.576E-04	44.589E-09						40
41	215.09	165.55	-481.48	-442.54	31.598	17.823E-02	-1.509E-04	43.417E-09						41
42			-221.06	-206.91	28.089	13.607E-02	-1.374E-04	50.702E-09	15.7565	2167.31	-43.15	-60	68	42
43			-284.70	-245.51	40.985	16.308E-02	-1.416E-04	41.462E-09	15.8516	2401.61	-36.30	-33	27	43
44	540.15	290.84	-100.48	-58.28	40.717	20.486E-02	-2.270E-04	88.425E-09	15.8742	2808.19	-45.99	-20	101	44
45			-933.66	-889.03	13.980	20.256E-02	-1.625E-04	45.134E-09	16.0543	1244.55	-13.06	-180	-125	45
46	94.06	48.90	-110.62	-137.37	30.869	-1.285E-02	27.892E-06	-1.272E-08	14.3686	530.22	-13.15	-210	-165	46
47			-138.50	-165.76	23.567	79.842E-03	-7.017E-05	24.535E-09						47
48	578.08	185.24	-393.77	-394.65	19.795	73.436E-03	-5.602E-05	17.153E-09	22.5898	3103.39	-0.16	-119	-69	48
49	274.08	200.22	117.15	66.95	27.444	81.266E-03	-7.666E-05	26.729E-09	15.9844	2690.85	-31.62	-45	69	49
50			-36.34						15.7078	3163.17	-72.18	101	30	50

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
51	CHCLF2	CHLORODIFLUOROMETHANE	86.469	-160.2	-40.8	369.2	49.8	0.165	1230	16	20,205	51
52	CHCL2F	DICHLOROFLUOROMETHANE	102.923	-135.2	8.8	451.6	51.7	0.197	1380	9	24,953	52
53	CHCL3	CHLOROFORM	119.378	-63.6	61.1	536.4	54.7	0.239	1489	20	29,726	53
54	CHN	HYDROGEN CYANIDE	27.026	-13.3	25.7	456.8	53.9	0.139	688	20	25,234	54
55	CH2BR2	DIBROMOMETHANE	173.835	-52.6	96.8	583.0	71.9		2500	20		55
56	CH2CL2	DICHLOROMETHANE	84.993	-95.1	39.8	510.0	60.8	0.193	1317	25	28,010	56
57	CH2O	FORMALDEHYDE	30.026	-117.2	-19.2	408.0	65.9		815	-20	23,027	57
58	CH2O2	FORMIC ACID	46.025	8.3	100.6	580.0			1226	15	21,939	58
59	CH3BR	METHYL BROMIDE	94.939	-93.7	3.5	464.0	86.1		1737	-5	23,928	59
60	CH3CL	METHYL CHLORIDE	50.488	-97.8	-24.3	416.3	66.8	0.139	915	20	21,436	60
61	CH3F	METHYL FLUORIDE	34.033	-141.8	-78.4	317.8	58.8	0.124	843	-60		61
62	CH3I	METHYL IODIDE	141.939	-66.5	42.4	528.0	65.9	0.190	2279	20	27,214	62
63	CH3NO2	NITROMETHANE	61.041	-28.6	101.2	588.0	63.1	0.173	1138	20	34,436	63
64	CH4	METHANE	16.043	-182.5	-161.5	190.6	46.0	0.099	425	-161	8185	64
65	CH4O	METHANOL	32.042	-97.7	64.6	512.6	81.0	0.118	791	20	35,278	65
66	CH4S	METHYL MERCAPTAN	48.107	-123.2	5.9	470.0	72.3	0.145	866	20	24,577	66
67	CH5N	METHYL AMINE	31.058	-93.5	-6.4	430.0	74.6	0.140	703	-14	26,000	67
68	CH6N2	METHYL HYDRAZINE	46.072		90.8	567.0	80.4	0.271				68
69	CH6SI	METHYL SILANE	46.145	-156.5	-57.6	352.5						69
70	C2CLF5	CHLOROPENTAFLUOROETHANE	154.467	-106.2	-39.2	353.2	31.6	0.252			19,469	70
71	C2CL2F4	1,1-DICHLORO-1,2,2,2-TETRAFLUOROETHANE	170.992	-94.2	3.8	418.6	33.0	0.294	1455	25		71
72	C2CL2F4	1,2-DICHLORO-1,1,2,2-TETRAFLUOROETHANE	170.922	-93.9	3.7	418.9	32.6	0.293	1480	4	23,279	72
73	C2CL3F3	1,2-DICHLORO-1,1,2,2-TETRAFLUOROETHANE	187.380	-35.0	47.5	487.2	34.1	0.304	1580	16	27,507	73
74	C2CL4	TETRACHLOROETHYLENE	165.834	-22.2	121.1	620.0	44.6	0.290	1620	20	34,750	74
75	C2CL4F2	1,1,2,2-TETRACHLORO-1,2-DIFLUOROETHANE	203.831	24.8	91.5	551.0			1645	25		75
76	C2F4	TETRAFLUOROETHYLENE	100.016	-142.5	-75.7	306.4	39.4	0.175	1519	-76		76
77	C2F6	HEXAFLUOROETHANE	138.012	-100.8	-78.3	292.8		0.224	1590	-78	16,161	77
78	C2N2	CYANOGEN	52.035	-27.9	-20.7	400.0	59.8					78
79	C2HCL3	TRICHLOROETHYLENE	131.389	-116.4	87.2	571.0	49.1	0.256	1462	20	31,401	79
80	C2HF3O2	TRIFLUOROACETIC ACID	114.024	-15.3	72.4	491.3	32.6		1535	0		80
81	C2H2	ACETYLENE	26.038	-80.8	-84.0	308.3	61.4	0.113	615	-84	16,957	81
82	C2H2F2	1,1-DIFLUOROETHYLENE	64.035			302.8	44.6	0.154				82
83	C2H2O	KETENE	42.038	-135.2	-41.2	380.0	64.8	0.145			20,641	83
84	C2H3CL	VINYL CHLORIDE	62.499	-153.8	-13.4	429.7	56.0	0.169	969	-14	20,641	84
85	C2H3CLF2	1-CHLORO-1,1-DIFLUOROETHANE	100.490	-131.2	-9.8	410.2	41.2	0.231	1100	30		85
86	C2H3CLO	ACETYL CHLORIDE	78.498	-113.0	50.7	508.0	58.8	0.204	1104	20	28,680	86
87	C2H3CL3	1,1,2-TRICHLOROETHANE	133.400	-36.7	113.7	602.0	41.5	0.294	1441	20	33,327	87
88	C2H3F	VINYL FLUORIDE	46.044	-143.2	-37.7	327.8	52.4	0.144				88
89	C2H3F3	1,1,1-TRIFLUOROETHANE	84.041	-111.3	-47.7	346.2	37.6	0.221			19,176	89
90	C2H3N	ACETONITRILE	41.053	-43.9	81.6	548.0	48.3	0.173	782	20	31,401	90
91	C2H3NO	METHYL ISOCYANATE	57.052		38.8	491.0	55.7		958	20	29,601	91
92	C2H4	ETHYLENE	28.054	-169.2	-103.8	282.4	50.4	0.129	577	-110	13,553	92
93	C2H4CL2	1,1-DICHLOROETHANE	98.960	-97.0	57.2	523.0	50.7	0.240	1168	25	28,721	93
94	C2H4CL2	1,2-DICHLOROETHANE	98.960	-35.7	83.4	561.0	53.7	0.220	1250	16	32,029	94
95	C2H4F2	1,1-DIFLUOROETHANE	66.051	-117.0	-24.8	386.6	45.0	0.181			21,353	95
96	C2H4O	ACETALDEHYDE	44.054	-123.0	20.4	461.0	55.7	0.154	778	20	25,749	96
97	C2H4O	ETHYLENE OXIDE	44.054	-112.2	10.3	469.0	71.9	0.140	899	0	25,623	97
98	C2H4O2	ACETIC ACID	60.052	16.6	117.9	594.4	57.9	0.171	1049	20	23,697	98
99	C2H4O2	METHYL FORMATE	60.052	-99.0	31.7	487.2	60.0	0.172	974	20	28,219	99
100	C2H5BR	ETHYL BROMIDE	108.966	-118.6	38.3	503.8	62.3	0.215	1451	25	26,502	100

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
51			-502.00	-470.89	17.300	16.182E-02	-1.170E-04	30.585E-09	15.5602	1704.80	-41.30	-48	-33	51
52			-298.94	-268.37	23.664	15.814E-02	-1.200E-04	32.636E-09						52
53	394.81	246.50	-101.32	-68.58	24.003	18.933E-02	-1.841E-04	66.570E-09	15.9732	2696.79	-46.16	-13	97	53
54	194.70	145.31	130.63	120.20	21.863	60.625E-03	-4.961E-05	18.154E-09	16.5138	2585.80	-37.15	-39	57	54
55	428.91	294.57	-4.19	-5.61										55
56	359.55	225.13	-95.46	-68.91	12.954	16.232E-02	-1.302E-04	42.077E-09	16.3029	2622.44	-41.70	-44	59	56
57	319.83	171.35	-115.97	-109.99	23.475	31.568E-03	29.852E-06	-2.300E-08	16.4775	2204.13	-30.15	-88	-2	57
58	729.35	325.72	-378.86	-351.23	11.715	13.578E-02	-8.411E-05	20.168E-09	16.9882	3599.58	-26.09	-2	136	58
59	298.15	211.15	-37.68	-28.18	14.428	10.911E-02	-5.401E-05	95.836E-10	16.0252	2271.71	-34.83	-58	53	59
60	426.45	193.56	-86.37	-62.93	13.875	10.140E-02	-3.889E-05	25.665E-10	16.1052	2077.97	-29.55	-93	-7	60
61			-234.04	-210.14	13.825	86.164E-03	-2.071E-05	-1.985E-09	16.3428	1704.41	-19.27	-132	-64	61
62	336.19	229.95	13.98	15.66	10.806	13.892E-02	-1.041E-04	34.855E-09	16.0905	2629.55	-36.50	-13	52	62
63	452.80	261.21	-74.78	-6.95	7.423	19.778E-02	-1.081E-04	20.850E-09	16.2193	2972.64	-64.15	5	136	63
64	114.14	57.60	-74.86	-50.87	19.251	52.126E-03	11.974E-06	-1.132E-08	15.2243	597.84	-7.16	-180	-153	64
65	555.30	260.64	-201.30	-162.62	21.152	70.924E-03	25.870E-06	-2.852E-08	18.5875	3626.55	-34.29	-16	91	65
66			-22.99	-9.92	13.268	14.566E-02	-8.545E-05	20.750E-09	16.1909	2338.38	-34.44	-73	27	66
67	311.80	176.30	-23.03	32.28	11.476	14.273E-02	-5.334E-05	47.520E-10	17.2622	2484.83	-32.92	-61	38	67
68			85.41	177.98					15.1424	2319.84	-91.70	-3	127	68
69														69
70					27.834	34.918E-02	-2.891E-04	81.391E-09	15.7343	1848.90	-30.88	-98	-43	70
71					40.453	32.783E-02	-2.752E-04	78.209E-09						71
72			-898.49		38.778	34.399E-02	-2.950E-04	85.076E-09						72
73			-745.67		61.140	28.742E-02	-2.420E-04	69.040E-09	15.8424	2532.61	-45.67	-23	87	73
74	392.58	281.82	-12.14	22.61	45.971	22.554E-02	-2.294E-04	83.820E-09	16.1642	3259.29	-52.15	34	187	74
75														75
76			-659.00	-624.13	29.010	22.772E-02	-2.037E-04	67.784E-09	15.8800	1574.60	-27.22	-133	-63	76
77			-1343.96	-1258.22	26.816	34.579E-02	-2.869E-04	81.350E-09	15.6422	1512.94	-26.94	-103	-73	77
78			309.15	297.39	35.935	92.528E-03	-8.223E-05	29.496E-09						78
79	145.67	196.60	-5.86	19.89	30.174	22.868E-02	-2.229E-04	82.438E-09	16.1827	3028.13	-43.15	-13	127	79
80														80
81			226.88	209.34	26.821	75.781E-03	-5.007E-05	14.122E-09	16.3481	1637.14	-19.77	-79	-71	81
82			-345.41	-321.71	3.073	24.447E-02	-2.099E-04	70.213E-09						82
83			-61.13	-60.33	6.385	16.383E-02	-1.084E-04	26.984E-09	16.0197	1849.21	-35.15	-103	-18	83
84	276.90	167.04	35.17	51.54	5.949	20.193E-02	-1.536E-04	47.730E-09	14.9601	1803.84	-43.15	-88	17	84
85					16.818	27.566E-02	-1.992E-04	53.047E-09						85
86			-244.09	-206.37	25.020	17.107E-02	-9.856E-05	22.190E-09	15.7514	2447.33	-55.53	-36	82	86
87	346.72	304.43	-138.58	-77.54	6.322	34.307E-02	-2.958E-04	97.929E-09	16.0381	3110.79	-56.16	29	155	87
88														88
89			-746.09	-679.22	5.744	31.409E-02	-2.597E-04	84.155E-09	15.8965	1814.91	-29.92	-3	27	89
90	334.91	210.05	87.92	105.67	20.482	10.831E-02	-4.492E-05	32.029E-10	16.2874	2945.47	-49.15	-13	117	90
91	616.78	227.47	-90.02		35.764	10.396E-02	-5.820E-06	-1.687E-08	16.3258	2480.37	-56.31	-43	67	91
92	168.98	93.94	52.33	68.16	3.806	15.659E-02	-8.348E-05	17.551E-09	15.5368	1347.01	-18.15	-153	-91	92
93	412.27	239.10	-130.00	-73.14	12.472	26.959E-02	-2.050E-04	63.011E-09	16.0842	2697.29	-45.03	-31	79	93
94	473.95	277.98	-129.79	-73.90	20.486	23.103E-02	-1.438E-04	33.888E-09	16.1764	2927.17	-50.22	-33	100	94
95	319.27	186.56	-494.04	-436.52	8.675	23.957E-02	-1.457E-04	33.942E-09	16.1871	2095.35	-29.16	-35	0	95
96	368.70	192.82	-166.47	-133.39	7.716	18.225E-02	-1.007E-04	23.802E-09	16.2418	2465.15	-37.15	-63	47	96
97	341.88	194.22	-52.67	-13.10	-7.519	22.224E-02	-1.256E-04	25.916E-09	16.7400	2567.61	-29.01	-73	37	97
98	600.94	306.21	-435.13	-376.94	4.840	25.485E-02	-1.753E-04	49.488E-09	16.8080	3405.57	-56.34	17	157	98
99	363.19	212.70	-350.02	-297.39	1.432	27.001E-02	-1.949E-04	57.024E-09	16.5104	2590.87	-42.60	-48	51	99
100	369.80	220.68	-64.06	-26.33	6.657	23.480E-02	-1.472E-04	38.041E-09	15.9338	2511.68	-41.44	-47	60	100

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
101	C2H5CL	ETHYL CHLORIDE	64.515	-136.4	12.2	460.4	52.7	0.199	896	20	24,702	101
102	C2H5F	ETHYL FLUORIDE	48.060	-143.3	-37.8	375.3	50.3	0.169				102
103	C2H5N	ETHYLENE IMIDE	43.069	-78.2	56.6				833	25	32,071	103
104	C2H5NO2	NITROETHANE	75.068	-89.2	114.0	595.0	48.5	0.228	1047	20	35,994	104
105	C2H6	ETHANE	30.070	-183.3	-88.7	305.4	48.8	0.148	548	-90	14,717	105
106	C2H6O	DIMETHYL ETHER	46.069	-141.5	-24.9	400.0	53.7	0.178	667	20	21,520	106
107	C2H6O	ETHANOL	46.069	-114.1	78.3	516.2	63.8	0.167	789	20	38,770	107
108	C2H6O2	ETHYLENE GLYCOL	62.069	-13.0	197.2	645.0	77.0	0.186	1114	20	52,544	108
109	C2H6S	ETHYL MERCAPTAN	62.134	-147.9	35.0	499.0	54.9	0.207	839	20	26,796	109
110	C2H6S	DIMETHYL SULPHIDE	62.130	-98.3	37.3	503.0	55.3	0.201	848	20	26,963	110
111	C2H7N	ETHYL AMINE	45.085	-81.2	16.5	456.0	56.2	0.178	683	20	28,052	111
112	C2H7N	DIMETHYL AMIDE	45.085	-92.2	6.8	437.6	53.1	0.187	656	20	26,502	112
113	C2H7NO	MONOETHANOLAMINE	61.084	10.3	170.3	614.0	44.6	0.196	1016	20	50,242	113
114	C2H8N2	ETHYLENEDIAMINE	60.099	10.8	117.2	593.0	62.8	0.206	896	20	41,868	114
115	C3H3N	ACRYLONITRILE	53.064	-83.7	77.3	536.0	35.5	0.210	806	20	32,657	115
116	C3H4	PROPADIENE	40.065	-136.3	-34.5	393.0	54.7	0.162	658	-35	18,631	116
117	C3H4	METHYL ACETYLENE	40.065	-102.7	-23.2	402.4	56.2	0.164	706	-50	22,148	117
118	C3H4O	ACROLEIN	56.064	-87.2	52.8	506.0	51.7		839	20	28,345	118
119	C3H4O2	ACRYLIC ACID	72.064	11.8	140.8	615.0	56.7	0.210	1051	20	46,055	119
120	C3H4O2	VINYL FORMATE	72.064	-57.7	46.4	475.0	57.8	0.210	963	20	32,155	120
121	C3H5CL	ALLYL CHLORIDE	76.526	-134.5	45.1	514.0	47.6	0.234	937	20	27,110	121
122	C3H5CL3	1:2:3-TRICHLOROPROPANE	147.432	-14.7	155.8	651.0	39.5	0.348	1389	20	38,435	122
123	C3H5N	PROPIONITRILE	55.080	-92.7	97.3	564.4	41.8	0.230	782	20	32,280	123
124	C3H6	CYCLOPROPANE	42.081	-127.5	-32.8	397.8	54.9	0.170	563	15	20,055	124
125	C3H6	PROPYLENE	42.081	-185.3	-47.8	365.0	46.2	0.181	612	-50	18,422	125
126	C3H6CL2	1:2-DICHLOROPROPANE	112.987	-100.5	96.3	577.0	44.6	0.226	1150	20	31,401	126
127	C3H6O	ACETONE	58.080	-95.0	56.2	508.1	47.0	0.209	790	20	29,140	127
128	C3H6O	ALLYL ALCOHOL	58.080	-129.2	96.8	545.0	57.1	0.203	855	15	39,984	128
129	C3H6O	PROPIONALDEHYDE	58.080	-80.2	47.8	496.0	47.6	0.223	797	20	28,303	129
130	C3H6O	PROPYLENE OXIDE	58.080	-112.2	34.3	482.2	49.2	0.186	829	20	27,005	130
131	C3H6O	VINYL METHYL ETHER	58.080	-121.7	4.8	436.0	47.6	0.205	750	20	19,050	131
132	C3H6O2	PROPIONIC ACID	74.080	-20.7	140.8	612.0	53.7	0.230	993	20	32,238	132
133	C3H6O2	ETHYL FORMATE	74.080	-79.4	54.2	508.4	47.4	0.229	927	16	30,145	133
134	C3H6O2	METHYL ACETATE	74.080	-98.2	56.9	506.8	46.9	0.228	934	20	30,145	134
135	C3H7CL	PROPYL CHLORIDE	78.542	-122.8	46.4	503.0	45.8	0.254	891	20	27,256	135
136	C3H7CL	ISOPROPYL CHLORIDE	78.452	-117.2	35.7	485.0	47.2	0.230	862	20	26,293	136
137	C3H8	PROPANE	44.097	-187.7	-42.1	369.8	42.5	0.203	582	-42	18,786	137
138	C3H8O	N-PROPYL ALCOHOL	60.096	-126.3	97.2	536.7	51.7	0.219	804	20	41,784	138
139	C3H8O	ISOPROPYL ALCOHOL	60.096	-88.5	82.2	508.3	47.6	0.220	786	20	39,858	139
140	C3H8O	METHYL ETHYL ETHER	60.096	-139.2	7.3	437.8	44.0	0.221	700	20	24,702	140
141	C3H8O2	METHYLAL	76.096	-105.2	41.8	497.0			888	18		141
142	C3H8O2	1:2-PROPANEDIOL	76.096	-60.2	187.3	625.0	60.8	0.237	1036	20	54,177	142
143	C3H8O2	1:3-PROPANEDIOL	76.096	-26.8	214.4	658.0	59.8	0.241	1053	20	56,522	143
144	C3H8O3	GLYCEROL	92.095	17.8	289.8	726.0	66.9	0.255	1261	20	61,127	144
145	C3H8S	METHYL ETHYL SULPHIDE	76.157	-106.0	66.6	533.0	42.6		837	20	29,517	145
146	C3H9N	N-PROPYL AMINE	59.112	-83.2	48.6	497.0	47.4	0.233	717	20	29,726	146
147	C3H9N	ISOPROPYL AMINE	59.112	-95.3	32.4	476.0	50.7	0.229	688	20	27,214	147
148	C3H9N	TRIMETHYL AMINE	59.112	-117.2	2.9	433.2	40.7	0.254	633	20	24,116	148
149	C4H2O3	MALEIC ANHYDRIDE	98.058	52.8	199.6				1310	60		149
150	C4H4	VINYL ACETYLENE	52.076	-45.6	4.9	455.0	49.6	0.202	710	0	24,493	150

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
101	320.94	190.83	-111.79	-60.04	-0.553	26.063E-02	-1.840E-04	55.475E-09	15.9800	2332.01	-36.48	-73	37	101
102			-261.67	-209.67	4.346	21.801E-02	-1.166E-04	24.103E-09	16.0686	1966.89	-27.00	-103	-21	102
103			123.51	178.11	-20.771	30.225E-02	-2.063E-04	56.480E-09	16.4227	2610.44	-63.15	-25	86	103
104			-101.32						17.4716	3848.24	-31.96	114	-21	104
105	156.60	95.57	-84.74	-32.95	5.409	17.811E-02	-6.938E-05	87.127E-10	15.6637	1511.42	-17.16	-143	-74	105
106			-184.18	-113.00	17.015	17.907E-02	-5.233E-05	-1.918E-09	16.8467	2361.44	-17.10	-94	-8	106
107	686.64	300.88	-234.96	-168.39	9.014	21.407E-02	-8.390E-05	13.733E-10	18.9119	3803.98	-41.68	-3	96	107
108	1365.00	402.41	-389.58	-304.67	35.697	24.832E-02	-1.497E-04	30.103E-09	20.2501	6022.18	-28.25	91	221	108
109	419.60	206.21	-46.14	-4.69	14.922	23.509E-02	-1.369E-04	31.619E-09	16.0077	2497.23	-41.77	-49	57	109
110	267.34	184.24	-37.56	6.95	24.304	18.748E-02	-6.875E-05	40.989E-10	16.0001	2511.56	-42.35	-47	58	110
111	340.54	192.44	-46.05	37.30	3.693	27.516E-02	-1.583E-04	38.083E-09	17.0073	2616.73	-37.30	-58	43	111
112			-18.84	68.04	-0.172	26.955E-02	-1.329E-04	23.392E-09	16.2653	2358.77	-35.15	-55	37	112
113	1984.10	367.03	-201.72		9.311	30.095E-02	-1.818E-04	46.557E-09	17.8174	3988.33	-86.93	71	204	113
114	839.76	316.41			38.297	24.070E-02	-4.338E-05	-3.948E-08	16.4082	3108.49	-72.15	19	152	114
115	343.31	210.42	185.06	195.44	10.693	22.077E-02	-1.565E-04	46.013E-09	15.9253	2782.21	-51.15	-18	112	115
116			192.26	202.52	9.906	19.774E-02	-1.182E-04	27.821E-09	13.1563	1054.72	-77.08	-99	-16	116
117			185.56	194.56	14.708	18.644E-02	-1.174E-04	32.243E-09	15.6227	1850.66	-44.07	-90	-6	117
118	388.17	217.14	-70.92	-65.19	11.970	21.055E-02	-1.071E-04	19.058E-09	15.9057	2606.53	-45.15	-38	87	118
119	733.02	307.15	-336.45	-286.25	1.742	31.908E-02	-2.352E-04	69.752E-09	16.5617	3319.18	-80.15	-42	177	119
120	428.40	224.83			27.813	18.388E-02	-3.560E-05	-2.335E-07	16.6531	2569.68	-63.15	-33	77	120
121	368.27	210.61	-0.63	43.63	2.529	30.467E-02	-2.278E-04	72.934E-09	15.9772	2531.92	-47.15	-43	77	121
122	818.63	342.88	-185.89	-97.85	26.883	36.220E-02	-2.787E-04	87.881E-09	16.1246	3417.27	-69.15	42	197	122
123	366.77	225.86	50.66	96.21	15.403	22.454E-02	-1.100E-04	19.540E-09	15.9571	2940.86	-55.15	-3	132	123
124			53.34	104.46	-35.240	38.133E-02	-2.881E-04	90.351E-09	15.8599	1971.04	-26.65	-93	-28	124
125	273.84	131.63	20.43	62.76	3.710	23.454E-02	-1.160E-04	22.048E-09	15.7027	1807.53	-26.15	-113	-33	125
126	514.36	281.03	-165.80	-83.15	10.450	36.547E-02	-2.604E-04	77.414E-09	16.0385	2985.07	-52.16	15	135	126
127	367.25	209.68	-217.71	-153.15	6.301	26.059E-02	-1.253E-04	20.377E-09	16.6513	2940.46	-35.93	-32	77	127
128	793.52	307.26	-132.09	-71.30	-1.105	31.464E-02	-2.032E-04	53.214E-09	16.9066	2928.20	-85.15	13	127	128
129	343.44	219.33	-192.17	-130.54	11.723	26.142E-02	-1.300E-04	21.261E-09	16.2315	2659.02	-44.15	-38	77	129
130	377.43	213.36	-92.82	-25.79	-8.457	32.569E-02	-1.989E-04	48.232E-09	15.3227	2107.58	-64.87	-48	67	130
131	318.41	180.98			15.629	23.413E-02	-9.697E-05	10.622E-09	14.4602	1980.22	-25.15	-83	42	131
132	535.04	299.32	-455.44	-369.57	5.669	36.890E-02	-2.865E-04	98.767E-09	17.3789	3723.42	-67.48	42	177	132
133	400.91	226.23	-371.54		24.673	23.161E-02	-2.120E-05	-5.359E-08	16.1611	2603.30	-54.15	-33	87	133
134	408.62	224.03	-409.72		16.550	22.454E-02	-4.342E-05	29.144E-09	16.1295	2601.92	-56.15	-28	87	134
135	374.77	215.00	-130.21	-50.70	-3.345	36.258E-02	-2.508E-04	74.483E-09	15.9594	2581.48	-42.95	-43	77	135
136	306.25	212.24	-146.54	-62.55	1.842	34.876E-02	-2.244E-04	58.615E-09	16.0384	2490.48	-43.15	-48	67	136
137	222.67	133.41	-103.92	-23.49	-4.224	30.626E-02	-1.586E-04	32.146E-09	15.7260	1872.46	-25.16	-109	-24	137
138	951.04	327.83	-256.57	-161.90	2.470	33.252E-02	-1.855E-04	42.957E-09	17.5439	3166.38	-80.15	12	127	138
139	1139.70	323.44	-272.60	-173.50	32.427	18.862E-02	64.058E-06	-9.261E-08	18.6929	3640.20	-53.54	0	111	139
140	303.82	171.66	-216.58	-117.73	18.669	26.854E-02	-1.025E-04	89.514E-10	13.5435	1161.63	-112.40	-68	37	140
141									15.8237	2415.92	-52.58	-3	42	141
142	1404.20	426.74	-424.25		0.632	42.119E-02	-2.981E-04	89.514E-09	20.5324	6091.95	-22.46	84	210	142
143	1813.00	406.96	-409.09		8.269	36.756E-02	-2.162E-04	50.535E-09	17.2917	3888.84	-123.20	107	252	143
144	3337.10	406.00	-585.31		8.424	44.422E-02	-3.159E-04	93.784E-09	17.2392	4487.04	-140.20	167	327	144
145			-59.66	11.43	19.527	28.906E-02	-1.209E-04	12.866E-09	15.9765	2722.95	-48.37	-23	87	145
146			-72.43	39.82	6.691	34.985E-02	-1.822E-04	35.864E-09	15.9957	2551.72	-49.15	-38	77	146
147	433.64	228.46	-83.82		-7.486	41.755E-02	-2.826E-04	83.485E-09	16.3637	2582.35	-40.15	-34	64	147
148			-23.86	98.98	-8.206	39.716E-02	-2.189E-04	46.222E-09	16.0499	2230.51	-39.15	-58	32	148
149	952.48	365.81			-13.075	34.847E-02	-2.184E-04	48.399E-09	16.2747	3765.65	-82.15	79	243	149
150			304.80	306.18	6.757	28.407E-02	-2.265E-04	74.609E-09	16.0100	2203.57	-43.15	-73	32	150



NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
151	C4H4O	FURAN	68.075	-85.7	31.3	490.2	55.0	0.218	938	20	27,105	151
152	C4H4S	THIOPHENE	84.136	-38.3	84.1	579.4	56.9	0.219	1071	16	31,485	152
153	C4H5CL	CHLOROPRENE	88.537		59.4	511.2	42.5	0.266	958	20	29,658	153
154	C4H5CL	CHLOROBUTADIENE	88.537	-60.0	67.8	527.2	39.5	0.265	963	20	29,038	154
155	C4H5N	ALLYL CYANIDE	67.091	-86.5	118.8	585.0	39.5	0.265	835	20	34,332	155
156	C4H5N	PYRROLE	67.091		129.8	640.0			967	21		156
157	C4H6	ETHYLACETYLENE	54.092	-125.8	8.0	463.7	47.1	0.220	650	16	24,995	157
158	C4H6	DIMETHYL ACETYLENE	54.092	-32.3	27.0	488.6	50.9	0.221	691	20	26,670	158
159	C4H6	1:2-BUTADIENE	54.092	-136.2	10.8	443.7	45.0	0.219	652	20	24,283	159
160	C4H6	1:3-BUTADIENE	54.092	-108.9	-4.5	425.0	43.3	0.221	621	20	22,483	160
161	C4H6O2	VINYL ACETATE	86.091	-100.2	72.8	525.0	43.6	0.265	932	20		161
162	C4H6O3	ACETIC ANHYDRIDE	102.089	-74.2	138.8	569.0	46.8	0.290	1087	20	41,240	162
163	C4H6O4	DIMETHYL OXALATE	118.090	53.8	163.4	628.0	39.8		1150	15		163
164	C4H6O4	SUCCINIC ACID	118.090	182.8	234.8							164
165	C4H7N	BUTYRONITRILE	69.107	-112.2	117.8	582.2	37.9	0.285	792	20	34,415	165
166	C4H7O2	METHYL ACRYLATE	86.091	-76.5	80.3	536.0	42.6	0.265	956	20	32,029	166
167	C4H8	1-BUTENE	56.108	-185.4	-6.3	419.6	37.2	0.240	595	20	21,930	167
168	C4H8	CIS-2-BUTENE	56.108	-138.9	3.7	435.6	42.0	0.234	621	20	23,362	168
169	C4H8	TRANS-2-BUTENE	56.108	-105.6	0.8	428.6	41.0	0.238	604	20	22,772	169
170	C4H8	CYCLOBUTANE	56.108	-90.8	12.5	459.9	49.9	0.210	694	20	24,200	170
171	C4H8	ISOBUTYLENE	56.108	-140.4	-6.9	417.9	40.0	0.239	594	20	22,131	171
172	C4H8O	N-BUTYRALDEHYDE	72.107	-96.4	74.8	524.0	40.5	0.278	802	20	31,527	172
173	C4H8O	ISOBUTYRALDEHYDE	72.107	-65.0	63.8	513.0	41.5	0.274	789	20	31,401	173
174	C4H8O	MERTYL ETHYL KETONE	72.107	-86.7	79.6	535.6	41.5	0.267	805	20	31,234	174
175	C4H8O	TETRAHYDROFURAN	72.107	-108.5	65.9	540.2	51.9	0.224	889	20	29,601	175
176	C4H8O	VINYL ETHYL ETHER	72.107	-115.3	35.6	475.0	40.7	0.260	793	20	26,502	176
177	C4H8O2	N-BUTYRIC ACID	88.107	-5.3	163.2	628.0	52.7	0.292	958	20	42,035	177
178	C4H8O2	1:4-DIOXANE	88.107	11.8	101.3	587.0	52.1	0.238	1033	20	36,383	178
179	C4H8O2	ETHYL ACETATE	88.107	-83.6	77.1	523.2	38.3	0.286	901	20	32,238	179
180	C4H8O2	ISOBUTYRIC ACID	88.107	-46.0	154.7	609.0	40.5	0.292	968	20	41,156	180
181	C4H8O2	METYL PROPIONATE	88.107	-87.5	79.8	530.6	40.0	0.282	915	20	32,573	181
182	C4H8O2	N-PROPYL FORMATE	88.107	-92.9	80.5	538.0	40.6	0.285	911	16	32,490	182
183	C4H9CL	1-CHLOROBUTANE	92.569	-123.1	78.4	542.0	36.9	0.312	886	20	30,019	183
184	C4H9CL	2-CHLOROBUTANE	92.569	-131.4	68.2	520.6	39.5	0.305	873	20	29,224	184
185	C4H9CL	2-CHLORO-2-METHYL PROPANE	92.569	-25.4	50.8	507.0	39.5	0.295	842	20	27,424	185
186	C4H9N	PYRROLIDINE	71.123		86.5	568.6	56.1	0.249	852	22		186
187	C4H9NO	MORPHOLINE	87.122	-4.8	128.2	618.0	54.7	0.253	1000	20	37,681	187
188	C4H10	N-BUTANE	58.124	-138.4	-0.5	425.2	38.0	0.255	579	20	22,408	188
189	C4H10	ISOBUTANE	58.124	-159.6	-11.9	408.1	36.5	0.263	557	20	21,311	189
190	C4H10O	N-BUTANOL	74.123	-89.3	117.7	562.9	44.2	0.274	810	20	43,124	190
191	C4H10O	2-BUTANOL	74.123	-114.7	99.5	536.0	41.9	0.268	807	20	40,821	191
192	C4H10O	ISOBUTANOL	74.123	-108.0	107.8	547.7	43.0	0.273	802	20	42,077	192
193	C4H10O	2-METHYL-2-PROPANOL	74.123	25.6	82.4	506.2	39.7	0.275	787	20	39,063	193
194	C4H10O	ETHYL ETHER	74.123	-116.3	34.5	466.7	36.4	0.280	713	20	26,712	194
195	C4H10O2	1:2-DIMETHOXYETHANE	90.123	-71.2	85.4	536.0	38.7	0.271	867	20	31,443	195
196	C4H10O3	DIETHYLENE GLYCOL	106.122	-8.2	245.8	681.0	46.6	0.316	1116	20	57,234	196
197	C4H10S	DIMETHYL SULPHIDE	90.184	-104.0	92.1	557.0	39.6	0.318	837	20	31,778	197
198	C4H10S2	DIETHYL DISULPHIDE	122.244	-101.5	154.0	642.0			998	20	37,723	198
199	C4H11N	N-BUTYL AMINE	73.139	-49.1	77.4	524.0	41.5	0.288	739	20	32,113	199
200	C4H11N	ISOBUTYL AMINE	73.139	-85.2	67.4	516.0	42.6	0.284			30,982	200

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
151	389.40	222.70	-34.71	0.88	-35.529	43.208E-02	-3.455E-04	10.743E-08	16.0612	244.70	-45.41	-35	90	151
152	498.60	264.90	115.81	126.86	-30.606	44.799E-02	-3.772E-04	12.527E-08	16.0243	2869.07	-51.80	-13	107	152
153			65.86						14.4844	1938.59	-85.36	27	-84	153
154			79.97											154
155	521.30	252.03			21.700	25.715E-02	-1.192E-04	12.292E-09	16.0019	3128.75	-58.15	127	157	155
156			108.35						16.7966	3457.47	-62.73	57	167	156
157			165.29	202.22	12.548	27.436E-02	-1.545E-04	34.499E-09	16.0605	2271.42	-40.30	-73	27	157
158			146.41	185.56	15.927	23.815E-02	-1.070E-04	17.534E-09	16.2821	2536.78	-37.34	-33	47	158
159			162.32	198.58	11.200	27.235E-02	-1.468E-04	30.890E-09	16.1039	2397.26	-30.88	-28	32	159
160	300.59	163.12	110.24	150.77	-1.687	34.185E-02	-2.340E-04	63.346E-09	15.7727	2142.66	-34.30	-58	17	160
161	457.89	235.35	-316.10		15.160	27.951E-02	-8.805E-05	-1.660E-08	16.1003	2744.68	-56.15	-18	106	161
162	502.33	286.04	-576.10	-477.00	-23.128	50.870E-02	-3.580E-04	98.348E-09	16.3982	3287.56	-75.11	35	164	162
163														163
164	0.00					15.072E+00	46.892E-03	-3.143E-04						164
165	438.04	256.84	34.08	108.73	15.211	32.058E-02	-1.638E-04	29.823E-09	16.2092	3202.21	-56.16	34	160	165
166	451.02	245.30			15.165	27.959E-02	-8.805E-05	-1.660E-08	16.1088	2788.43	-59.15	-13	117	166
167	256.30	151.86	-0.13	71.34	-2.994	35.320E-02	-1.982E-04	44.631E-09	15.7564	2132.42	-33.15	-83	22	167
168	268.94	155.34	-6.99	65.90	0.440	29.534E-02	-1.018E-04	-6.155E-10	15.8171	2210.71	-36.15	-73	32	168
169	259.01	153.30	-11.18	63.01	18.317	25.636E-02	-7.013E-05	-8.989E-09	15.8177	2212.32	-33.15	-73	27	169
170			26.67	110.11	-50.254	50.242E-02	-3.558E-04	10.471E-08	15.9254	2359.09	-31.78	-73	17	170
171			-16.91	58.11	16.052	28.043E-02	-1.091E-04	90.979E-10	15.7528	2125.75	-33.15	-83	17	171
172	472.31	233.42	-205.15	-114.84	14.080	34.570E-02	-1.723E-04	28.872E-09	16.1668	2839.09	-50.15	-18	107	172
173	464.06	253.64	-215.87	-121.42	24.463	33.557E-02	-2.057E-04	63.681E-09	15.9888	2676.98	-51.15	-26	97	173
174	423.84	231.67	-238.52	-146.16	10.944	35.592E-02	-1.900E-04	39.197E-09	16.5986	3150.42	-36.65	-16	103	174
175	419.79	244.46	-184.34		-19.104	51.623E-02	-4.132E-04	14.541E-08	16.1069	2768.38	-46.90	-3	97	175
176	349.95	189.02	-140.26		17.279	32.360E-02	-1.471E-04	21.495E-09	15.8911	2449.26	-44.15	-48	67	176
177	640.42	321.13	-476.16		11.740	41.370E-02	-2.430E-04	55.308E-09	17.9240	4130.93	-70.55	62	197	177
178	660.36	308.77	-315.27	-180.91	-53.574	59.871E-02	-4.085E-04	10.622E-08	16.1327	2966.88	-62.15	2	137	178
179	427.38	235.98	-443.21	-327.62	7.235	40.717E-02	-2.092E-04	28.546E-09	16.1516	2790.50	-57.15	-13	112	179
180	588.65	311.24	-484.25		9.814	46.683E-02	-3.720E-04	13.502E-08	16.7792	3385.49	-94.15	57	192	180
181	442.88	238.39			18.204	31.397E-02	-9.353E-05	-1.828E-08	16.1693	2804.06	-58.92	-13	112	181
182	452.97	246.09							15.7671	2593.95	-69.69	7	87	182
183	783.72	260.03	-147.38	-38.81	-2.613	44.966E-02	-2.937E-04	80.805E-09	15.9750	2826.26	-49.05	-18	112	183
184	480.77	237.30	-161.61	-53.51	-3.433	45.594E-02	-2.981E-04	82.564E-09	15.9907	2753.43	-47.15	-23	102	184
185	543.41	253.35	-183.38	-64.14	-3.931	46.515E-02	-2.886E-04	78.712E-09	15.8121	2567.15	-44.15	-38	87	185
186			-3.60	114.76	-51.531	53.382E-02	-3.240E-04	75.279E-09	15.9444	2717.03	-67.90	27	127	186
187	914.14	332.75			-42.802	53.884E-02	-2.666E-04	41.994E-09	16.2364	3171.35	-71.15	27	167	187
188	265.84	160.20	-126.23	-17.17	9.487	33.130E-02	-1.108E-04	-2.822E-09	15.6782	2154.90	-34.42	-78	7	188
189	302.51	170.20	-134.61	20.89	-1.390	38.473E-02	-1.846E-04	28.952E-09	15.5381	2032.73	-33.15	-86	7	189
190	984.54	341.12	-274.86	-150.89	3.266	41.801E-02	-2.242E-04	46.850E-09	17.2160	3137.02	-94.43	15	131	190
191	1441.70	331.50	-292.82	-167.72	5.753	42.454E-02	-2.328E-04	47.730E-09	17.2102	3026.03	-86.65	25	120	191
192	1199.10	343.85	-283.40	-167.43	-7.708	46.892E-02	-2.884E-04	72.306E-09	16.8712	2874.73	-100.30	20	115	192
193	972.10	363.38	-312.63	-177.77	-48.613	71.720E-02	-7.084E-04	29.199E-08	16.8548	2658.29	-95.50	20	103	193
194	353.14	190.58	-252.38	-122.42	21.424	33.587E-02	-1.035E-04	-9.357E-09	16.0828	2511.29	-41.95	-48	67	194
195					32.234	35.672E-02	-1.336E-04	83.987E-10	16.0241	2869.79	-53.15	-11	120	195
196	1943.00	385.24	-571.50		73.060	34.441E-02	-1.468E-04	18.464E-09	17.0326	4122.52	-122.50	129	287	196
197	407.59	233.32	-83.53	17.79	13.595	39.595E-02	-1.780E-04	26.490E-09	15.9531	2896.27	-54.49	-13	117	197
198			-74.69	22.27	26.896	46.013E-02	-2.710E-04	59.704E-09	16.0607	3421.57	-64.19	39	182	198
199	472.06	243.98	-92.11	49.24	5.079	44.757E-02	-2.407E-04	75.990E-09	16.6085	3012.70	-48.96	-14	100	199
200					9.491	44.296E-02	-2.110E-04	23.329E-09	16.1419	2704.16	-56.15	-22	100	200

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
201	C4H11N	DIETHYL AMINE	73.139	-49.8	55.4	496.6	37.1	0.301	707	20	27,842	201
202	C4H12SI	TETRAMETHYLSILANE	88.225	-102.2	27.6	448.6	28.2	0.362	646	20	24,685	202
203	C5H4O2	FURFURAL	96.085	-31.0	161.7	657.1	49.2	0.270	1156	25		203
204	C5H5N	PYRIDINE	79.102	-41.7	115.3	620.0	56.3	0.254	983	20	35,169	204
205	C5H8	CYCLOPENTENE	68.119	-135.1	44.2	506.0			772	20	27,005	205
206	C5H8	1;2-PENTADIENE	68.119	-137.3	44.8	503.0	40.7	0.276	693	20	27,591	206
207	C5H8	1-TRANS-3-PENTADIENE	68.119	-87.5	42.0	496.0	39.9	0.275	676	20	27,047	207
208	C5H8	1;4-PENTADIENE	68.119	-148.3	25.9	478.0	37.9	0.276	661	20	25,163	208
209	C5H8	1-PENTYNE	68.119	-105.7	40.1	493.4	40.5	0.278	690	20		209
210	C5H8	2-METHYL-1;3-BUTADIENE	68.119	-146.0	34.0	484.0	38.5	0.276	681	20	26,084	210
211	C5H8	3-METHYL-1;2-BUTADIENE	68.119	-113.7	40.8	496.0	41.1	0.267	686	20	27,256	211
212	C5H8O	CYCLOPENTONE	84.118	-50.7	130.7	626.0	53.7	0.268	950	20	36,593	212
213	C5H8O2	ETHYL ACRYLATE	100.118	-72.2	99.8	552.0	37.5	0.320	921	20	33,285	213
214	C5H10	CYCLOPENTANE	70.135	-93.9	49.2	511.6	45.1	0.260	745	20	27,315	214
215	C5H10	1-PENTENE	70.135	-165.3	29.9	464.7	40.5	0.300	640	20	25,213	215
216	C5H10	CIS-2-PENTENE	70.135	-151.4	36.9	476.0	36.5	0.300	656	20	26,126	216
217	C5H10	TRANS-2-PENTENE	70.135	-140.3	36.3	475.0	36.6	0.300	649	20	26,084	217
218	C5H10	2-METHYL-1-BUTENE	70.135	-137.6	31.1	465.0	34.5	0.294	650	20	25,514	218
219	C5H10	2-METHYL-2-BUTENE	70.135	-133.8	38.5	470.0	34.5	0.318	662	20	26,322	219
220	C5H10	3-METHYL-1-BUTENE	70.135	-168.5	20.1	450.0	35.2	0.300	627	20	24,116	220
221	C5H10O	VALERALDEHYDE	86.134	-91.2	102.8	554.0	35.5	0.333	810	20	33,662	221
222	C5H10O	METHYL N-PROPYL KETONE	86.134	-77.2	102.3	564.0	38.9	0.301	806	20	33,494	222
223	C5H10O	METHYL ISOPROPYL KETONE	86.134	-92.2	94.2	553.4	38.5	0.310	803	20	30,647	223
224	C5H10O	DIETHYL KETONE	86.134	-39.0	101.9	561.0	37.4	0.336	814	20	33,746	224
225	C5H10O2	N-VALERIC ACID	102.134	-34.2	185.5	651.0	38.5	0.340	939	20	49,823	225
226	C5H10O2	ISOBUTYL FORMATE	102.134	-95.2	98.4	551.0	38.8	0.350	885	20	34,206	226
227	C5H10O2	N-PROPYL ACETATE	102.134	-95.2	101.6	549.4	33.3	0.345	887	20	34,206	227
228	C5H10O2	ETHYL PROPIONATE	102.134	-73.9	98.8	546.0	33.6	0.345	895	16	34,248	228
229	C5H10O2	METHYL BUTYRATE	102.134	-84.8	102.6	554.4	34.8	0.340	898	20	34,101	229
230	C5H10O2	METHYL ISOBUTYRATE	102.134	-87.8	92.2	540.8	34.3	0.339	891	20	33,386	230
231	C5H11N	PIPERIDINE	85.150	-10.5	106.5	594.0	47.6	0.289	862	20	34,248	231
232	C5H12	N-PENTANE	72.151	-129.8	36.0	469.6	33.7	0.304	626	20	25,791	232
233	C5H12	2-METHYL BUTANE	72.151	-159.3	27.8	460.4	33.8	0.306	620	20	24,702	233
234	C5H12	2;2-DIMETHYL PROPANE	72.151	-16.6	9.4	433.8	32.0	0.303	591	20	22,768	234
235	C5H12O	1-PENTANOL	88.150	-78.2	137.8	586.0	38.5	0.326	815	20	44,380	235
236	C5H12O	2-METHYL-1-BUTANOL	88.150	-70.2	128.7	571.0	38.5	0.322	819	20	45,217	236
237	C5H12O	3-METHYL-1-BUTANOL	88.150	-117.2	131.2	579.5	38.5	0.329	810	20	44,129	237
238	C5H12O	2-METHYL-2-BUTANOL	88.150	-8.8	102.0	545.0	39.5	0.319	809	20	40,612	238
239	C5H12O	2;2-DIMETHYL-1-PROPANOL	88.150	53.8	113.1	549.0	39.5	0.319	783	54	43,124	239
240	C5H12O	ETHYL PROPYL ETHER	88.150	-126.8	63.6	500.6	32.5		733	20	30,522	240
241	C5H12O	METHYL-T-BUTYL ETHER	88.150	-108.2	55.1	407.1	34.3	0.339	741	20	27,646	241
242	C5H12O	BUTYLMETHYL ETHER	88.150	-115.5	70.1	512.8	34.3	0.329				242
243	C6F6	PERFLUOROBENZENE	186.056		80.2	516.7	33.0					243
244	C6F12	PERFLUOROCYCLOHEXANE	300.047		52.5	457.2	24.3					244
245	C6F14	PERFLUORO-N-HEXANE	338.044	-87.2	57.1	451.7	19.0	0.442				245
246	C6H3CL3	1;2;4-TRICHLOROBENZENE	181.449	16.8	213.0	734.9	39.8	0.401				246
247	C6H4CL2	O-DICHLOROBENZENE	147.004	-17.1	180.4	697.3	41.0	0.360	1306	20	39,691	247
248	C6H4CL2	M-DICHLOROBENZENE	147.004	-24.8	172.8	684.0	38.5	0.359	1288	20	38,644	248
249	C6H4CL2	P-DICHLOROBENZENE	147.004	53.1	174.1	685.0	39.5	0.372	1248	55	38,812	249
250	C6H5BR	BROMOBENZENE	157.010	-30.9	156.0	670.0	45.2	0.324	1495	20		250

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
201	473.89	229.29	-72.43	72.14	2.039	44.296E-02	-2.183E-04	36.530E-09	16.0545	2595.01	-53.15	-31	77	201
202			-232.41						16.0999	2570.24	-28.73	27	-84	202
203					18.196	28.198E-02	-6.523E-05	-5.476E-08	18.7949	5365.88	5.40	77	277	203
204	618.50	291.58	140.26	190.33	39.791	49.279E-02	-3.558E-04	10.044E-08	16.0910	3095.13	-61.15	12	152	204
205	396.83	218.66	32.95	110.66	-41.512	46.306E-02	-2.579E-04	54.345E-09	15.9356	2583.07	-39.70	-29	105	205
206			145.70	210.55	8.826	38.799E-02	-2.280E-04	52.461E-09	15.9297	2544.34	-44.30	-23	67	206
207			77.87	146.83	30.689	28.110E-02	-6.711E-05	-2.352E-08	15.9182	2541.69	-41.43	-23	67	207
208			105.51	170.36	6.996	39.515E-02	-2.374E-04	55.978E-09	15.7392	2344.02	-41.69	-33	47	208
209			144.44	210.39	18.066	35.035E-02	-1.913E-04	40.976E-09	16.0429	2515.62	-45.97	-43	62	209
210	328.49	182.48	75.78	145.95	-34.122	45.845E-02	-3.337E-04	10.002E-08	15.8548	2467.40	-39.64	-23	57	210
211			129.79	198.75	14.687	35.977E-02	-1.976E-04	42.622E-09	15.9880	2541.83	-42.26	-23	62	211
212	574.71	303.44	-192.76		-40.641	52.251E-02	-3.035E-04	71.301E-09	16.0897	3193.92	-66.15	27	167	212
213	438.08	256.84			16.810	36.898E-01	-1.382E-04	-5.732E-09	16.0890	2974.94	-58.15	1	136	213
214	406.69	231.67	-77.29	38.64	-53.625	54.261E-02	-3.031E-04	64.854E-09	15.8574	2588.48	-41.79	-43	72	214
215	305.25	174.70	-20.93	79.17	-0.134	43.292E-02	-2.317E-04	46.808E-09	15.7646	2405.96	-39.63	-53	52	215
216	305.31	175.72	-28.09	71.89	-13.151	46.013E-02	-2.541E-04	54.554E-09	15.8251	2459.05	-42.56	-53	57	216
217	349.33	176.62	-31.78	69.96	1.947	41.818E-02	-2.178E-04	44.045E-09	15.9011	2495.97	-40.18	-53	57	217
218	369.27	193.39	-36.34	65.65	10.572	39.971E-02	-1.946E-04	33.139E-09	15.8260	2426.42	-40.36	-53	52	218
219	322.47	180.43	-42.58	59.70	11.803	35.090E-02	-1.117E-04	-5.807E-09	15.9238	2521.53	-40.31	-47	62	219
220			-28.97	74.82	21.742	38.895E-02	-2.007E-04	40.105E-09	15.7179	2333.61	-36.33	-63	42	220
221	521.30	252.03	-227.97	-108.35	14.239	43.292E-02	-2.107E-04	31.623E-09	16.1623	3030.20	-58.15	-46	139	221
222	437.94	243.03	-258.83	-137.16	1.147	48.023E-02	-2.818E-04	66.612E-09	16.0031	2934.87	-62.25	2	137	222
223					-2.914	49.907E-02	-2.935E-04	66.654E-09	14.1779	1993.12	-103.20	-2	133	223
224	409.17	236.65	-258.83	135.36	30.011	39.394E-02	-1.907E-04	33.976E-09	16.8138	3410.51	-40.15	2	127	224
225	729.09	341.13	-490.69	-357.43	13.389	50.325E-02	-2.931E-04	66.193E-09	17.6306	4092.15	-86.55	77	222	225
226					19.850	40.336E-02	-1.436E-04	-7.402E-09	16.2292	2980.47	-64.15	5	136	226
227	489.53	255.83	-466.03		15.420	45.008E-02	-1.686E-04	-1.439E-08	16.2291	2980.47	-64.15	7	137	227
228	463.31	248.72	-470.18	-323.72	19.854	40.344E-02	-1.437E-04	-7.402E-09	16.1620	2935.11	-64.16	3	123	228
229	479.35	254.66												229
230	451.21	246.09												230
231	772.79	313.49	-49.03		-53.068	62.886E-02	-3.358E-04	64.267E-09	16.1004	3015.46	-61.15	7	143	231
232	313.66	182.48	-146.54	-8.37	-3.626	48.734E-02	-2.580E-04	53.047E-09	15.8333	2477.07	-39.94	-53	57	232
233	367.32	191.58	-154.58	-14.82	-9.525	50.660E-02	-2.729E-04	57.234E-09	15.6338	2348.67	-40.05	-57	49	233
234	355.54	196.35	-166.09	-15.24	-16.592	55.517E-02	-3.306E-04	76.325E-09	15.2069	2034.15	-45.37	-13	32	234
235	1151.10	349.62	-298.94	-146.12	3.869	50.451E-02	-2.639E-04	51.205E-09	16.5270	3026.89	-105.00	37	138	235
236	1259.40	349.85	-302.71	-165.71	-9.483	56.773E-02	-3.481E-04	86.374E-09	16.2708	2752.19	-116.30	34	129	236
237	1148.80	349.51	-302.29		-9.542	56.815E-02	-3.485E-04	86.499E-09	16.7127	3026.43	-104.10	25	153	237
238	1502.00	336.75	-329.92	-165.38	-12.087	60.960E-02	-4.204E-04	12.284E-08	15.0113	1988.08	-137.80	25	102	238
239			-293.08	-125.52	12.154	53.968E-02	-3.160E-04	71.217E-09	18.1336	3694.96	-65.00	55	133	239
240	399.87	213.39							15.3549	2423.41	-62.28	-27	87	240
241			-292.99	-125.52	2.533	51.372E-02	-2.596E-04	43.040E-09	16.4174	2913.70	-30.63	-88	88	241
242									15.8830	2666.26	-53.70	69	23	242
243			-957.27	-879.98	36.283	52.670E-02	-4.547E-04	14.558E-08	16.1940	2827.53	-57.66	-3	117	243
244									13.9087	1374.07	-136.80	7	127	244
245									15.8307	2488.59	-59.73	-3	57	245
246					-14.361	60.876E-02	-5.623E-04	20.725E-08	16.8979	4452.50	-53.00	127	327	246
247	554.35	319.07	29.98	82.73	-14.302	55.056E-02	-4.513E-04	14.294E-08	16.2799	3798.23	-59.84	58	210	247
248	402.20	300.89	26.46	78.63	-13.590	54.931E-02	-4.505E-04	14.269E-08	16.8173	4104.13	-43.15	53	202	248
249	483.82	312.03	23.03	77.20	-14.344	55.349E-02	-4.559E-04	14.478E-08	16.1135	3626.83	-64.64	54	204	249
250	508.18	302.42	105.09	138.62	-28.805	53.507E-02	-4.080E-04	12.117E-08	15.7972	3313.00	-67.71	47	177	250

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
251	C6H5CL	CHLOROBENZENE	112.559	-45.6	131.7	632.4	45.2	0.308	1106	20	36,572	251
252	C6H5F	FLUOROBENZENE	96.104	-39.2	85.3	560.1	45.5	0.271	1024	20		252
253	C6H5I	IODOBENZENE	204.011	-31.4	188.2	721.0	45.2	0.351	1855	4	39,523	253
254	C6H5NO2	NITROBENZENE	123.112	4.8	210.6	712.0	35.0	0.337	1203	20	44,031	254
255	C6H6	BENZENE	78.114	5.5	80.1	562.1	48.9	0.259	885	16	30,781	255
256	C6H6O	PHENOL	94.113	40.8	181.8	694.2	61.3	0.229	1059	40	45,636	256
257	C6H7N	ANILINE	93.129	-6.2	184.3	699.0	53.1	0.270	1022	20	41,868	257
258	C6H7N	4-METHYL PYRIDINE	93.129	3.7	145.3	646.0	44.6	0.311	955	20	37,472	258
259	C6H10	1,5-HEXADIENE	82.146	-141.2	59.4	507.0	34.5	0.328	692	20	27,470	259
260	C6H10	CYCLOHEXENE	82.146	-103.5	82.9	560.4	43.5	0.292	816	16	30,480	260
261	C6H10O	CYCLOHEXANONE	98.145	-31.2	155.6	629.0	38.5	0.312	951	15	39,775	261
262	C6H12	CYCLOHEXANE	84.162	6.5	80.7	553.4	40.7	0.308	779	20	29,977	262
263	C6H12	METHYLCYCLOPENTANE	84.162	-142.5	71.8	532.7	37.9	0.319	754	16	29,098	263
264	C6H12	1-HEXENE	84.162	-139.9	63.4	504.0	31.7	0.350	673	20	28,303	264
265	C6H12	CIS-2-HEXENE	84.162	-141.2	68.8	518.0	32.8	0.351	687	20	29,140	265
266	C6H12	TRANS-2-HEXENE	84.162	-133.2	67.8	516.0	32.7	0.351	678	20	28,931	266
267	C6H12	CIS-3-HEXENE	84.162	-137.9	66.4	517.0	32.8	0.350	680	20	28,721	267
268	C6H12	TRANS-3-HEXENE	84.162	-113.5	67.1	519.9	32.5	0.350	677	20	28,973	268
269	C6H12	2-METHYL-2-PENTENE	84.162	-135.1	67.3	518.0	32.8	0.351	691	16	29,015	269
270	C6H12	3-METHYL-CIS-2-PENTENE	84.162	-134.9	67.7	518.0	32.8	0.351	694	20	28,847	270
271	C6H12	3-METHYL-TRANS-2-PENTENE	84.162	-138.5	70.4	521.0	32.9	0.350	698	20	29,308	271
272	C6H12	4-METHYL-CIS-2-PENTENE	84.162	-134.2	56.4	490.0	30.4	0.360	669	20	27,591	272
273	C6H12	4-METHYL-TRANS-2-PENTENE	84.162	-141.2	58.5	493.0	30.4	0.360	669	20	27,968	273
274	C6H12	2,3-DIMETHYL-1-BUTENE	84.162	-157.3	55.6	501.0	32.4	0.343	678	20	27,424	274
275	C6H12	2,3-DIMETHYL-2-BUTENE	84.162	-74.3	73.2	524.0	33.6	0.351	708	20	29,655	275
276	C6H12	3,3-DIMETHYL-1-BUTENE	84.162	-115.2	41.2	490.0	32.5	0.340	653	20	25,665	276
277	C6H12O	CYCLOHEXANOL	100.161	24.8	161.1	625.0	37.5	0.327	942	30	45,511	277
278	C6H12O	METHYL ISOBUTYL KETONE	100.161	-84.2	116.4	571.0	32.7	0.371	801	20	35,588	278
279	C6H12O2	N-BUTYL ACETATE	116.160	-73.5	126.0	579.0	31.4	0.400	898	0	36,006	279
280	C6H12O2	ISOBUTYL ACETATE	116.160	-98.9	116.8	561.0	30.4	0.414	875	20	35,873	280
281	C6H12O2	ETHYL BUTYRATE	116.160	-93.2	120.8	566.0	31.4	0.395	879	20	34,332	281
282	C6H12O2	ETHYL ISOBUTYRATE	116.160	-88.2	111.0	553.0	30.4	0.410	869	20	35,023	282
283	C6H12O2	N-PROPYL PROPIONATE	116.160	-75.9	122.5	578.0	30.4	0.390	881	20	36,383	283
284	C6H14	N-HEXANE	86.178	-95.4	68.7	507.4	29.7	0.370	659	20	28,872	284
285	C6H14	2-METHYL PENTANE	86.178	-153.7	60.2	497.5	30.1	0.367	653	20	27,800	285
286	C6H14	3-METHYL PENTANE	86.178	-118.2	63.2	504.4	31.2	0.367	664	20	28,093	286
287	C6H14	2,2-DIMETHYL BUTANE	86.178	-99.9	49.7	488.7	30.8	0.359	649	20	26,322	287
288	C6H14	2,3-DIMETHYL BUTANE	86.178	-128.6	58.0	499.9	31.3	0.358	662	20	27,298	288
289	C6H14O	1-HEXANOL	102.177	-44.0	157.0	610.0	40.5	0.381	819	20	48,567	289
290	C6H14O	ETHYL BUTYL ETHER	102.177	-103.2	92.2	531.0	30.4	0.390	749	20	31,820	290
291	C6H14O	DIISOPROPYL ETHER	102.177	-85.5	68.3	500.0	28.8	0.386	724	20	29,349	291
292	C6H15N	DIPROPYLAMINE	101.193	-63.2	109.2	550.0	31.4	0.407	738	20	37,011	292
293	C6H15N	TRIETHYLAMINE	101.193	-114.8	89.5	535.0	30.4	0.390	728	20	31,401	293
294	C7F14	PERFLUOROMETHYLCYCLOHEXANE	350.055		76.3	486.8	23.3					294
295	C7F16	PERFLUORO-N-HEPTANE	388.051	-78.2	82.5	474.8	16.2	0.664	1733	20		295
296	C7H5N	BENZONITRILE	103.124	-13.2	190.8	699.4	42.2		1010	15		296
297	C7H6O	BENZALDEHYDE	106.124	-57.2	178.8	695.0	46.6		1045	20	42,705	297
298	C7H6O2	BENZOIC ACID	122.124	122.4	249.8	752.0	45.6	0.341	1075	130	50,660	298
299	C7H7NO2	O-NITROTOLUENE	137.139	-9.2	222.1	720.0	34.0	0.371	1167	20	45,487	299
300	C7H7NO2	M-NITROTOLUENE	137.139	16.0	233.1	725.0	30.5	0.371	1158	20	46,090	300

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
251	477.76	276.22	51.87	99.23	-33.888	56.312E-02	-4.522E-04	14.264E-08	16.0676	3295.12	-55.60	47	147	251
252	452.06	252.89	-116.64	-69.08	-38.728	56.689E-02	-4.434E-04	13.553E-08	16.5487	3181.78	-37.59	-23	97	252
253	565.72	331.21	162.66	187.90	-29.274	55.643E-02	-4.509E-04	14.432E-08	16.1454	3776.53	-64.38	17	197	253
254			-67.49						16.1484	4032.66	-71.81	44	211	254
255	545.64	265.34	82.98	129.75	-33.917	47.436E-02	-3.017E-04	71.301E-09	15.9008	2788.51	-52.36	7	104	255
256	1405.50	370.07	-96.67	-32.91	-35.843	59.829E-02	-4.827E-04	15.269E-08	16.4279	3490.89	-98.59	72	208	256
257	1074.60	357.21	86.92	166.80	-40.516	63.849E-02	-5.133E-04	16.333E-08	16.6748	3857.52	-73.15	67	227	257
258	500.97	285.50	102.28		-17.430	48.818E-02	-2.798E-04	54.512E-09	16.2143	3409.40	-62.65	27	187	258
259			83.74						16.1351	2728.54	-45.45	9	77	259
260	506.92	264.54	-5.36	106.93	-68.651	72.515E-02	-5.414E-04	16.442E-08	15.8243	2813.53	-49.98	27	87	260
261	787.38	336.47	-230.27	-90.81	-37.807	55.391E-02	-1.953E-04	-1.534E-08						261
262	653.62	290.84	-123.22	31.78	-54.541	61.127E-02	-2.523E-04	13.214E-09	15.7527	2766.63	-50.50	7	107	262
263	440.52	243.24	-105.93	35.80	-50.108	63.807E-02	-3.642E-04	80.135E-09	15.8023	2731.00	-47.11	-23	102	263
264	357.43	197.74	-41.70	87.50	-1.746	53.089E-02	-2.903E-04	60.541E-09	15.8089	2654.81	-47.30	-33	87	264
265	344.33	197.95	-52.38	76.28	-9.810	53.089E-02	-2.717E-04	48.274E-09	16.2057	2897.97	-39.30	-28	97	265
266	344.33	197.95	-53.925	76.49	-32.925	69.292E-02	-5.619E-04	20.046E-08	15.8727	2701.72	-48.62	-28	92	266
267	344.33	197.95	-47.65	83.07	-21.729	58.113E-02	-3.362E-04	74.567E-09	15.8384	2680.52	-48.40	-28	92	267
268	344.33	197.95	-54.47	77.67	-4.338	55.098E-02	-3.282E-04	80.470E-09	15.9288	2718.68	-47.77	-28	92	268
269			-59.79	71.26	-14.750	56.689E-02	-3.341E-04	79.633E-09	15.9423	2725.89	-47.64	-28	97	269
270			-57.78	73.27	-14.750	56.689E-02	-3.341E-04	79.633E-09	15.9124	2731.79	-46.76	-25	91	270
271			-58.70	71.34	-14.750	56.689E-02	-3.341E-04	79.633E-09	15.9484	2750.50	-48.33	-23	93	271
272			-50.37	82.19	-1.675	53.759E-02	-3.044E-04	67.533E-09	15.7527	2580.52	-46.56	-35	79	272
273			-54.39	79.67	12.627	51.540E-02	-3.007E-04	73.269E-09	15.8425	2631.57	-46.00	-33	81	273
274			-55.77	79.09	7.025	55.852E-02	-3.696E-04	10.630E-08	15.8012	2612.69	-43.78	-38	87	274
275			-59.24	75.91	2.294	48.274E-02	-2.199E-04	30.417E-09	16.0043	2798.63	-47.71	-23	102	275
276			-43.17	98.22	-12.556	54.847E-02	-2.915E-04	52.084E-09	15.3755	2326.80	-48.24	-48	67	276
277			-294.75	-117.98	-55.534	72.139E-02	-4.086E-04	82.354E-09						277
278	473.65	259.03	-284.03		3.894	56.564E-02	-3.318E-04	82.312E-09	15.7165	2893.66	-70.75	12	152	278
279	537.58	272.30	-486.76		13.620	54.889E-02	-2.278E-04	-7.913E-10	16.1836	3151.09	-69.15	22	162	279
280	533.99	270.49	-495.47		7.310	57.401E-02	-2.576E-04	11.011E-09	16.1714	3092.83	-66.15	16	154	280
281	489.95	264.22			21.508	49.279E-02	-1.938E-04	35.588E-10	15.9987	3127.60	-60.15	15	159	281
282														282
283									16.8641	3558.18	-47.86	19	147	283
284	362.79	207.09	-167.30	-0.25	-4.413	58.197E-02	-3.119E-04	64.937E-09	15.8366	2697.55	-48.78	-28	97	284
285	384.13	208.27	-174.42	-5.02	-10.567	61.839E-02	-3.573E-04	80.847E-09	15.7476	2614.38	-46.58	-33	97	285
286	372.11	207.55	-171.74	-2.14	-2.386	56.899E-02	-2.870E-04	50.325E-09	15.7701	2653.43	-46.02	-33	92	286
287	438.44	226.67	-185.68	-9.63	-16.634	62.928E-02	-3.481E-04	68.496E-09	15.5536	2489.50	-43.81	-43	77	287
288	444.19	228.86	-177.90	-4.10	-14.608	61.504E-02	-3.376E-04	68.203E-09	15.6802	2595.44	-44.25	-38	81	288
289	1179.40	354.94	-317.78	-135.65	4.811	58.908E-02	-3.010E-04	54.261E-09	18.0994	4055.45	-76.49	35	157	289
290	443.32	234.68			23.626	53.675E-02	-2.528E-04	41.567E-09	16.0477	2921.52	-55.15	-8	127	290
291	410.58	219.67	-319.03	-121.96	7.503	58.490E-02	-3.027E-04	58.448E-09	16.3417	2895.73	-43.15	-24	91	291
292	561.11	257.39			6.460	62.928E-02	-3.390E-04	70.715E-09	16.5939	3259.08	-55.15	29	149	292
293	355.52	214.48	-99.65	110.36	-18.430	71.552E-02	-4.392E-04	10.923E-08	15.8853	2882.38	-51.15	-13	127	293
294			-2898.10						15.7130	2610.57	-61.93	17	112	294
295			-3386.70	-3089.31					15.9747	2719.68	-64.50	-3	117	295
296			218.97	261.05	-26.004	57.317E-02	-4.430E-04	13.490E-08						296
297	686.84	314.66	-36.80	22.40	-12.142	49.614E-02	-2.845E-04	51.665E-09	16.3501	3748.62	-66.12	27	187	297
298	2617.60	407.88	-290.40	-210.55	-51.292	62.928E-02	-4.237E-04	10.622E-08	17.1634	4190.70	-125.20	132	287	298
299			-265.86						14.2028	2603.49	-151.52	222	129	299
300			-265.86											300

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
301	C7H7NO2	P-NITROTOLUENE	137.139	54.8	238.0	735.0	30.1	0.371	1164	20	46,875	301
302	C7H8	TOLUENE	92.141	-95.2	110.6	591.7	41.1	0.316	867	20	33,201	302
303	C7H8O	METHYL PHENYL ETHER	108.140	-37.5	153.6	641.0	41.7		996	20		303
304	C7H8O	BENZYL ALCOHOL	108.140	-15.4	205.4	677.0	46.6	0.334	1041	25	50,535	304
305	C7H8O	O-CRESOL	108.140	30.9	191.0	697.6	50.1	0.282	1028	40	45,217	305
306	C7H8O	M-CRESOL	108.140	12.2	202.2	705.8	45.6	0.310	1034	20	47,436	306
307	C7H8O	P-CRESOL	108.140	34.7	201.9	704.6	51.5		1019	40	47,478	307
308	C7H9N	2,3-DIMETHYLPYRIDINE	107.156		160.8	655.4			942	25		308
309	C7H9N	2,5-DIMETHYLPYRIDINE	107.156		157.0	644.2			938	0		309
310	C7H9N	3,4-DIMETHYLPYRIDINE	107.156		179.1	683.8			954	25		310
311	C7H9N	3,5-DIMETHYLPYRIDINE	107.156		171.9	667.2			939	25		311
312	C7H9N	METHYLPHENYLAMINE	107.156	-57.2	195.9	701.0	52.0		989	20		312
313	C7H9N	O-TOLUIDINE	107.156	-14.8	200.1	694.0	37.5	0.343	998	20	45,364	313
314	C7H9N	M-TOLUIDINE	107.156	-30.4	203.3	709.0	41.5	0.343	989	20	45,636	314
315	C7H9N	P-TOLUIDINE	107.156	43.7	200.1	667.0			964	50	44,799	315
316	C7H14	CYCLOHEPTANE	98.189	-8.2	118.7	589.0	37.2	0.390	810	20	33,076	316
317	C7H14	1,1-DIMETHYLCYCLOPENTANE	98.189	-69.8	87.8	547.0	34.5	0.360	759	16	30,312	317
318	C7H14	CIS-1,2-DIMETHYLCYCLOPENTANE	98.189	-53.9	99.5	564.8	34.5	0.368	777	16	31,719	318
319	C7H14	TRANS-1,2-DIMETHYLCYCLOPENTANE	98.189	-117.6	91.8	553.2	34.5	0.362	756	16	30,878	319
320	C7H14	ETHYLCYCLOPENTANE	98.189	-138.5	103.4	569.5	33.9	0.375	771	16	32,301	320
321	C7H14	METHYLCYCLOHEXANE	98.189	-126.6	100.9	572.1	34.8	0.368	774	16	31,150	321
322	C7H14	1-HEPTENE	98.189	-118.9	93.6	537.2	28.4	0.440	679	20	31,108	322
323	C7H14	2,3,3-TRIMETHYL-1-BUTENE	98.189	-109.9	77.8	533.0	29.0	0.400	705	20	28,889	323
324	C7H16	N-HEPTANE	100.250	-90.6	98.4	540.2	27.4	0.432	684	20	31,719	324
325	C7H16	2-METHYLHEXANE	100.205	-118.3	90.0	530.3	27.4	0.421	679	20	30,689	325
326	C7H16	3-METHYLHEXANE	100.205	-173.2	91.8	535.2	28.2	0.404	687	20	30,815	326
327	C7H16	2,2-DIMETHYLPENTANE	100.205	-123.8	79.2	520.4	27.8	0.416	674	20	29,182	327
328	C7H16	2,3-DIMETHYLPENTANE	100.205		89.7	537.3	29.1	0.393	965	20	30,409	328
329	C7H16	2,4-DIMETHYLPENTANE	100.205	-119.2	80.5	519.7	27.4	0.418	673	20	29,517	329
330	C7H16	3,3-DIMETHYLPENTANE	100.205	-134.5	86.0	536.3	29.5	0.414	693	20	29,668	330
331	C7H16	3-ETHYLPENTANE	100.205	-118.6	93.4	540.6	28.9	0.416	698	20	30,978	331
332	C7H16	2,2,3-TRIMETHYLBUTANE	100.205	-24.9	80.8	531.1	29.6	0.398	690	20	28,968	332
333	C7H16O	1-HEPTANOL	116.204	-34.0	176.3	633.0	30.4	0.435	822	20	48,148	333
334	C8H4O3	PHTHALIC ANHYDRIDE	148.118	130.8	286.8	810.0	47.6	0.368			49,614	334
335	C8H8	STYRENE	104.152	-30.7	145.1	647.0	39.9		906	20	36,844	335
336	C8H8O	METHYL PHENYL KETONE	120.151	19.6	201.7	701.0	38.5	0.376	1032	15		336
337	C8H8O2	METHYL BENZOATE	136.151	-12.4	199.0	692.0	36.5	0.396	1083	20	43,124	337
338	C8H10	O-XYLENE	106.168	-25.2	144.4	630.2	37.3	0.369	880	20	36,844	338
339	C8H10	M-XYLENE	106.168	-47.9	139.1	617.0	35.5	0.376	864	20	36,383	339
340	C8H10	P-XYLENE	106.168	13.2	138.3	616.2	35.2	0.379	861	20	36,006	340
341	C8H10	ETHYL BENZENE	106.168	-95.0	136.1	617.1	36.1	0.374	867	20	35,588	341
342	C8H10O	O-ETHYLPHENOL	122.167	-3.4	204.5	703.0			1037	0	48,106	342
343	C8H10O	M-ETHYLPHENOL	122.167	-4.2	218.4	716.4			1025	0	50,828	343
344	C8H10O	P-ETHYLPHENOL	122.167	44.8	217.8	716.4					50,660	344
345	C8H10O	ETHYL PHENYL ETHER	122.167	-30.2	169.8	647.0	34.2		979	4		345
346	C8H10O	2,3-XYLENOL	122.167	74.8	216.9	722.8					47,311	346
347	C8H10O	2,4-XYLENOL	122.167	24.8	210.8	707.6					47,143	347
348	C8H10O	2,5-XYLENOL	122.167	74.8	211.1	723.0					46,892	348
349	C8H10O	2,6-XYLENOL	122.167	48.8	200.9	701.0					44,380	349
350	C8H10O	3,4-XYLENOL	122.167	64.8	226.8	729.8					49,823	350

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
301									16.0433	3914.07	-90.45	233	129	301
302	467.33	255.24	50.03	122.09	-24.355	51.246E-02	-2.765E-04	49.111E-09	16.0137	3096.52	-53.67	7	137	302
303	388.84	325.85							16.2394	3430.82	-69.58	97	167	303
304	1088.00	367.21	-94.08		-7.398	54.805E-02	-3.357E-04	77.707E-09	17.4582	4384.81	-73.15	112	330	304
305	1533.40	365.61	-128.70	-37.10	-32.276	70.045E-02	-5.924E-04	21.240E-08	15.9148	3305.37	-108.00	97	207	305
306	1785.60	370.75	-123.43	-40.57	-45.008	72.641E-02	-6.029E-04	20.775E-08	17.2878	4274.42	-74.09	97	207	306
307	1826.90	372.68	-125.48	-30.90	-40.633	70.548E-02	-5.757E-04	19.674E-08	16.1989	3479.39	-111.30	97	207	307
308			68.29						17.1492	4219.74	-33.04	147	167	308
309			66.44						16.3046	3545.14	-63.59	77	162	309
310			70.05						16.9517	4237.04	-41.65	127	187	310
311			72.81						16.8850	4106.95	-44.45	127	187	311
312	915.12	332.74	85.41	199.33					16.3066	3756.28	-80.71	47	207	312
313	1085.10	356.46							16.7834	4072.58	-72.15	102	227	313
314	928.12	354.07			-15.989	56.815E-02	-3.033E-04	46.432E-09	16.7498	4080.32	-73.15	82	227	314
315	738.90	356.02							16.6968	4041.04	-72.15	77	227	315
316			-119.41	63.05	-76.187	78.670E-02	-4.204E-04	75.614E-09	15.7818	3066.05	-56.80	57	162	316
317			-138.37	39.06	-57.891	76.702E-02	-4.501E-04	10.103E-08	15.6973	2807.94	-51.20	-13	117	317
318			-129.62	45.76	-55.643	76.158E-02	-4.484E-04	10.140E-08	15.7729	2922.30	-52.94	-3	127	318
319			-136.78	38.39	-54.521	75.907E-02	-4.480E-04	10.170E-08	15.7594	2861.53	-51.46	-13	117	319
320	433.81	249.72	-127.15	44.59	-55.312	75.111E-02	-4.396E-04	10.040E-08	15.8581	2990.13	-52.47	-3	129	320
321	528.41	271.58	-154.87	27.30	-61.919	78.419E-02	-4.438E-04	93.659E-09	15.7105	2926.04	-51.75	-3	127	321
322	368.69	214.32	-62.34	95.88	-3.303	62.969E-02	-3.512E-04	76.074E-09	15.8894	2895.51	-53.97	-8	127	322
323			-86.54						15.6536	2719.47	-49.56	-20	102	323
324	436.73	232.53	-187.90	8.00	-5.146	67.617E-02	-3.651E-04	76.577E-09	15.8737	2911.32	-56.51	-3	127	324
325	417.46	225.13	-195.06	3.22	-39.389	86.416E-02	-6.289E-04	18.363E-08	15.8261	2845.06	-53.60	-9	117	325
326			-192.43	4.61	-7.046	68.370E-02	-3.734E-04	78.335E-09	15.8133	2855.66	-53.93	-8	117	326
327	417.37	226.19	-206.28	0.08	-50.099	89.556E-02	-6.360E-04	17.358E-08	15.6917	2740.15	-49.85	-19	105	327
328			-199.38	0.67	-7.046	70.476E-02	-3.734E-04	78.335E-09	15.7815	2850.64	-51.33	-11	115	328
329			-202.14	3.10	-7.046	68.370E-02	-3.734E-04	78.335E-09	15.7179	2744.78	-51.52	-17	105	329
330			-201.68	2.64	-7.046	68.370E-02	-3.734E-04	78.335E-09	15.7190	2829.10	-47.83	-13	112	330
331			-189.79	11.01	-7.046	68.370E-02	-3.734E-04	78.335E-09	15.8317	2882.44	-53.26	-7	119	331
332			-204.94	4.27	-22.944	75.195E-02	-4.421E-04	10.048E-08	15.6398	2764.40	-47.10	-19	106	332
333	1287.00	361.83	-332.01	-121.00	4.907	67.784E-02	-3.447E-04	60.457E-09	15.3068	2626.42	-146.60	60	176	333
334			-371.79		-4.455	65.398E-02	-4.283E-04	10.094E-08	15.9984	4467.01	-83.15	136	342	334
335	528.64	276.71	147.46	213.95	-28.248	61.588E-02	-4.023E-04	99.353E-09	16.0193	3328.57	-63.72	32	187	335
336	1316.40	310.82	-86.92	1.84	-29.580	64.100E-02	-4.071E-04	97.217E-09	16.2384	3781.07	-81.15	77	247	336
337	768.94	332.33	-254.06		-21.210	55.015E-02	-1.799E-04	44.254E-09	16.2272	3751.83	-81.15	77	243	337
338	513.54	277.98	19.01	122.17	-15.851	59.620E-02	-3.443E-04	75.279E-09	16.1156	3395.57	-59.46	32	172	338
339	453.42	257.18	17.25	118.95	-29.165	62.969E-02	-3.747E-04	84.783E-09	16.1390	3366.99	-58.04	27	167	339
340	475.16	261.40	17.96	121.21	-25.091	60.416E-02	-3.374E-04	68.203E-09	16.0963	3346.65	-57.84	27	167	340
341	472.82	264.22	29.81	130.67	-43.099	70.715E-02	-4.811E-04	13.008E-08	16.0195	3272.47	-59.95	27	177	341
342			-145.78						17.9610	4928.36	-45.75	77	227	342
343			-146.58						17.1955	4272.77	-86.08	97	227	343
344			-144.65						19.0905	5579.62	-44.15	97	227	344
345	646.88	305.91							16.1673	3473.20	-78.66	112	187	345
346			-157.34						16.2424	3724.58	-102.40	147	227	346
347			-162.78						13.2456	3655.26	-103.80	137	227	347
348			-161.53						16.2328	3667.32	-102.40	137	217	348
349			-161.95						16.2809	3749.53	-85.55	127	207	349
350			-156.50						16.3004	3733.53	-113.90	157	247	350



NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
351	C8H10O	3;5-XYLENOL	122.167	63.8	221.6	715.6					49,404	351
352	C8H11N	N,N-DIMETHYLANILINE	121.183	2.4	193.5	687.0	36.3		956	20		352
353	C8H16	1;1-DIMETHYLCYCLOHEXANE	112.216	-33.5	119.5	591.0	29.7	0.416	785	16	32,615	353
354	C8H16	CIS-1;2-DIMETHYLCYCLOHEXANE	112.216	-50.1	129.7	606.0	29.7		796	20	33,662	354
355	C8H16	TRANS-1;2-DIMETHYLCYCLOHEXANE	112.216	-88.2	123.4	596.0	29.7		776	20	32,908	355
356	C8H16	CIS-1;3-DIMETHYLCYCLOHEXANE	112.216	-75.6	120.1	591.0	29.7		766	20	32,825	356
357	C8H16	TRANS-1;3-DIMETHYLCYCLOHEXANE	112.216	-90.2	124.4	598.0	29.7		785	20	33,871	357
358	C8H16	CIS-1;4-DIMETHYLCYCLOHEXANE	112.216	-87.5	124.3	598.0	29.7		783	20	33,787	358
359	C8H16	TRANS-1;4-DIMETHYLCYCLOHEXANE	112.216	-37.0	119.3	590.0	29.7		763	20	32,615	359
360	C8H16	ETHYLCYCLOHEXANE	112.216	-111.4	131.7	609.0	30.3	0.450	788	20	34,332	360
361	C8H16	1;1;2-TRIMETHYLCYCLOPENTANE	112.216		113.7	579.5	29.4				32,615	361
362	C8H16	1;1;3-TRIMETHYLCYCLOPENTANE	112.216		104.8	569.5	28.3				31,694	362
363	C8H16	CIS;CIS;TRANS-1;2;4-TRIMETHYLCYCLOPENTANE	112.216		117.8	579.0	28.8				33,076	363
364	C8H16	CIS;TRANS;CIS-1;2;4-TRIMETHYLCYCLOPENTANE	112.216		109.2	571.0	28.1				33,076	364
365	C8H16	1-METHYL-1-ETHYLCYCLOPENTANE	112.216		121.5	592.0	29.9				33,662	365
366	C8H16	N-PROPYLCYCLOPENTANE	112.216	-117.4	130.9	603.0	30.0	0.425	781	16	34,131	366
367	C8H16	ISOPROPYLCYCLOPENTANE	112.216	-112.7	126.4	601.0	30.0		776	20	34,122	367
368	C8H16	1-OCTENE	112.216	-101.8	121.2	566.6	26.2	0.464	715	20	33,787	368
369	C8H16	TRANS-2-OCTENE	112.216	-87.8	124.9	580.0	27.7		720	20	34,332	369
370	C8H18	N-OCTANE	114.232	-56.8	125.6	568.8	24.8	0.492	703	20	34,436	370
371	C8H18	2-METHYLHEPTANE	114.232	-109.2	117.6	559.6	24.8	0.488	702	16	33,829	371
372	C8H18	3-METHYLHEPTANE	114.232	-120.5	118.9	563.6	25.4	0.464	706	20	33,913	372
373	C8H18	4-METHYLHEPTANE	114.232	-121.0	117.7	561.7	25.4	0.476	705	20	33,913	373
374	C8H18	2;2-DIMETHYLHEXANE	114.232	-121.2	108.8	549.8	25.3	0.478	695	20	32,280	374
375	C8H18	2;3-DIMETHYLHEXANE	114.232		115.6	563.4	26.2	0.468	712	20	33,226	375
376	C8H18	2;4-DIMETHYLHEXANE	114.232		109.4	553.5	25.5	0.472	700	20	32,615	376
377	C8H18	2;5-DIMETHYLHEXANE	114.232	-91.3	109.1	550.0	24.8	0.482	693	20	32,657	377
378	C8H18	3;3-DIMETHYLHEXANE	114.232	-126.2	111.9	562.0	26.5	0.443	710	20	32,490	378
379	C8H18	3;4-DIMETHYLHEXANE	114.232		117.7	568.8	27.0	0.466	719	20	33,298	379
380	C8H18	3-ETHYLHEXANE	114.232		118.5	565.4	26.0	0.455	718	16	33,633	380
381	C8H18	2;2;3-TRIMETHYLPENTANE	114.232	-112.3	109.8	563.4	27.3	0.436	716	20	32,029	381
382	C8H18	2;2;4-TRIMETHYLPENTANE	114.232	-107.4	99.2	543.9	25.6	0.468	692	20	31,028	382
383	C8H18	2;3;3-TRIMETHYLPENTANE	114.232	-100.7	114.7	573.5	28.2	0.455	726	20	32,364	383
384	C8H18	2;3;4-TRIMETHYLPENTANE	114.232	-109.3	113.4	566.3	27.3	0.461	719	20	32,753	384
385	C8H18	2-METHYL-3-ETHYLPENTANE	114.232	-115.0	115.6	567.0	27.1	0.443	719	20	32,988	385
386	C8H18	3-METHYL-3-ETHYLPENTANE	114.232	-90.9	118.2	576.5	28.1	0.455	727	20	32,816	386
387	C8H18O	1-OCTANOL	130.231	-15.5	195.2	658.0	34.5	0.490	826	20	50,660	387
388	C8H18O	2-OCTANOL	130.231	-32.0	179.7	637.0	27.4	0.494	821	20	44,380	388
389	C8H18O	2-ETHYLHEXANOL	130.231	-70.0	184.6	613.0	27.6	0.494	833	20	46,599	389
390	C8H18O	BUTYL ETHER	130.231	-97.9	142.4	580.0	25.3	0.500	768	20	37,263	390
391	C8H18O5	TETRAETHYLENE GLYCOL	194.229		318.9	795.8	21.0	0.646				391
392	C8H19N	DIBUTYLAMINE	129.247	-62.2	159.6	596.0	25.3	0.517	767	20	39,775	392
393	C8H20Si	TETRAETHYL SILANE	144.333	-82.5	153.4	603.7	26.0	0.582	766	20	36,473	393
394	C9H8	INDENE	116.163		181.9	691.9	38.2	0.377				394
395	C9H10	INDAN	118.179		177.0	681.1	36.3	0.392				395
396	C9H10	ALPHA-METHYL STYRENE	118.179		165.3	654.0	34.0	0.397	911	20	38,309	396
397	C9H10O2	ETHYL BENZOATE	150.178	-34.9	212.7	697.0	32.4	0.451	1046	20	44,799	397
398	C9H12	N-PROPYLBENZENE	120.195	-99.5	159.2	638.3	32.0	0.440	862	20	38,267	398
399	C9H12	ISOPROPYLBENZENE	120.195	-96.1	152.4	631.0	32.1	0.428	862	20	37,556	399
400	C9H12	1-METHYL-2-ETHYLBENZENE	120.195	-80.9	165.1	651.0	30.4	0.460	881	20	38,895	400

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
351			-161.48						16.4192	3775.91	-109.00	137	227	351
352	553.02	320.03	84.15	231.36					16.9647	4276.08	-52.80	72	207	352
353			-181.12	35.25	-72.105	89.974E-02	-5.020E-04	10.304E-08	15.6535	3043.34	-55.30	10	147	353
354			-172.29	41.24	-68.370	89.723E-02	-5.137E-04	10.986E-08	15.7438	3148.35	-57.31	17	157	354
355			-180.12	34.50	-68.479	91.230E-02	-5.355E-04	11.811E-08	15.7337	3117.43	-54.02	13	151	355
356			-184.89	29.85	-65.163	88.383E-02	-4.932E-04	10.199E-08	15.7470	3081.95	-55.08	11	147	356
357			-176.68	36.34	-64.154	88.258E-02	-5.016E-04	10.685E-08	15.7371	3093.95	-57.76	15	152	357
358			-176.77	37.97	-64.154	88.258E-02	-5.016E-04	10.685E-08	15.7333	3098.39	-57.00	14	152	358
359			184.72	31.74	-70.363	91.314E-02	-5.309E-04	11.547E-08	15.6984	3063.44	-54.57	10	147	359
360	506.43	280.76	-171.87	39.27	-63.891	88.928E-02	-5.108E-04	11.028E-08	15.8125	3183.25	-58.15	20	160	360
361									15.7084	3015.51	-54.59	6	141	361
362									15.6794	2938.09	-53.25	0	131	362
363									15.7543	3073.95	-54.20	10	145	363
364									15.7756	3009.70	-53.23	9	144	364
365									15.8222	3120.66	-55.06	13	149	365
366	454.23	264.22	-148.17	52.63	-55.973	84.490E-02	-4.924E-04	11.175E-08	15.8969	3187.67	-59.99	21	158	366
367									15.8561	3176.22	-55.18	16	154	367
368	418.82	237.63	-82.98	104.29	-4.099	72.390E-02	-4.036E-04	86.750E-09	15.9630	3116.52	-60.39	16	147	368
369	427.64	240.32	-94.58	92.74	-12.820	75.321E-02	-4.442E-04	10.505E-08	15.8554	3134.97	-58.00	16	152	369
370	473.70	251.71	-208.59	16.41	-6.096	77.121E-02	-4.195E-04	88.551E-09	15.9426	3120.29	-63.63	19	152	370
371	643.61	259.51	-215.62	12.77	-89.744	12.422E-01	-1.176E-03	46.180E-08	15.9278	3097.63	-59.46	12	144	371
372			-212.77	13.73	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8865	3065.96	-60.74	13	145	372
373			-212.23	16.75	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8893	3057.05	-60.59	12	144	373
374			-224.87	10.72	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7431	2932.56	-58.08	3	132	374
375			-214.07	17.71	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8189	3029.06	-58.99	10	142	375
376			-219.56	11.72	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7797	2965.44	-58.36	5	135	376
377			-222.78	10.47	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7954	2964.06	-58.74	5	135	377
378	446.20	244.67	-220.27	13.27	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7755	3011.51	-55.71	6	138	378
379			-213.15	17.33	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8415	3062.52	-58.29	11	144	379
380	437.60	238.33	-211.01	16.54	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8671	3057.57	-60.55	13	145	380
381	474.57	257.61	-220.27	17.12	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7162	2981.56	-54.73	4	136	381
382	467.04	246.43	-224.29	13.69	-7.461	77.791E-02	-4.287E-04	91.733E-09	15.6850	2896.28	-52.41	-4	125	382
383			-216.58	18.92	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7578	3057.94	-52.77	7	142	383
384			-217.59	18.92	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.7818	3028.09	-55.62	7	140	384
385			211.35	21.27	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8040	3035.08	-57.84	9	142	385
386			-215.12	19.93	-9.215	78.586E-02	-4.400E-04	96.966E-09	15.8126	3102.06	-53.47	10	145	386
387	1312.10	369.97	-360.06	-120.16	6.171	76.074E-02	-3.797E-04	62.635E-09	15.7428	3017.81	-137.10	70	195	387
388					25.879	76.409E-02	-4.224E-04	90.644E-09	14.7108	2441.66	-150.70	72	180	388
389	1798.00	351.17	-365.55		-14.993	86.541E-02	-5.280E-04	12.845E-08	15.3614	2773.46	-140.00	75	185	389
390	473.50	266.56	-334.11	-88.59	6.054	77.288E-02	-4.085E-04	80.847E-09	16.0778	3296.15	-66.15	32	182	390
391					7.164	86.164E-02	-2.904E-04	-9.115E-08	20.5564	8215.28	-11.50	227	427	391
392	581.42	286.54			9.764	80.805E-02	-4.392E-04	92.486E-09	16.7307	3721.90	-64.15	49	186	392
393			-314.93						16.6385	3873.18	-39.33	153	-1	393
394					-42.944	68.957E-02	-4.340E-04	91.482E-09	16.4380	3994.97	-49.40	77	277	394
395					-59.639	78.126E-02	-4.841E-04	98.474E-09	16.2601	3789.86	-57.00	77	277	395
396	354.34	270.80			-24.329	69.333E-02	-4.530E-04	11.807E-08	16.3308	3644.30	-67.15	75	220	396
397	746.50	338.47			20.670	68.873E-02	-3.608E-04	50.618E-09	16.2065	3845.09	-84.15	88	258	397
398	527.45	282.65	7.83	137.33	-31.288	74.860E-02	-4.601E-04	10.810E-08	16.0062	3433.84	-66.01	43	188	398
399	517.17	276.22	3.94	137.08	-39.364	78.419E-02	-5.087E-04	12.912E-08	15.9722	3363.60	-63.37	38	181	399
400			1.21	131.17	-16.446	69.961E-02	-4.120E-04	93.282E-09	16.1253	3535.33	-65.85	48	194	400

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
401	C9H12	1-METHYL-3-ETHYLBENZENE	120.195	-95.6	161.3	637.0	28.4	0.490	865	20	38,560	401
402	C9H12	1-METHYL-4-ETHYLBENZENE	120.195	-62.4	162.0	640.0	29.4	0.470	861	20	38,435	402
403	C9H12	1:2:3-TRIMETHYLBENZENE	120.195	-25.5	176.0	664.5	34.6	0.430	894	20	40,068	403
404	C9H12	1:2:4-TRIMETHYLBENZENE	120.195	-46.2	169.3	649.1	32.3	0.430	880	16	39,272	404
405	C9H12	1:3:5-TRIMETHYLBENZENE	120.195	-44.8	164.7	637.3	31.3	0.433	865	20	39,063	405
406	C9H18	N-PROPYLCYCLOHEXANE	126.243	-94.5	156.7	639.0	28.1		793	20	36,090	406
407	C9H18	ISOPROPYLCYCLOHEXANE	126.243	-89.8	154.5	640.0	28.4		802	20		407
408	C9H18	1-NONENE	126.243	-81.4	146.8	592.0	23.4	0.580	745	0	36,341	408
409	C9H20	N-NONANE	128.259	-53.5	150.8	594.6	23.1	0.548	718	20	36,940	409
410	C9H20	2:2:3-TRIMETHYLHEXANE	128.259		133.6	588.0	24.9				34,792	410
411	C9H20	2:2:4-TRIMETHYLHEXANE	128.259	-120.2	126.5	573.7	23.7		720	16	34,039	411
412	C9H20	2:2:5-TRIMETHYLHEXANE	128.259	-105.8	124.1	568.0	23.3	0.519	717	16	33,787	412
413	C9H20	3:3-DIMETHYLPENTANE	128.259		146.1	610.0	26.7		752	20	36,006	413
414	C9H20	2:2:3:3-TETRAMETHYLPENTANE	128.259		140.2	607.6	27.4				35,295	414
415	C9H20	2:2:3:4-TETRAMETHYLPENTANE	128.259		133.0	592.7	26.0				34,290	415
416	C9H29	2:2:4:4-TETRAMETHYLPENTANE	128.259	-67.2	122.2	574.7	24.8		719	20	32,866	416
417	C9H20	2:3:3:4-TETRAMETHYLPENTANE	128.259		141.5	607.6	27.2				34,960	417
418	C10H8	NAPHTHALENE	128.174	80.3	217.9	748.4	40.5	0.410	971	90	43,292	418
419	C10H12	1:2:3:4-TETRAHYDRONAPHTHALENE	132.206	-31.2	207.5	719.0	35.2		973	20	39,733	419
420	C10H14	N-BUTYLBENZENE	134.222	-88.0	183.2	660.5	28.9	0.497	860	20	39,272	420
421	C10H14	ISOBUTYLBENZENE	134.222	-51.5	172.7	650.0	31.4	0.480	853	20	37,849	421
422	C10H14	SEC-BUTYLBENZENE	134.222	-75.5	173.3	664.0	29.5		862	20	37,974	422
423	C10H14	TERT-BUTYLBENZENE	134.222	-57.9	169.1	660.0	29.7		867	20	37,639	423
424	C10H14	1-METHYL-2-ISOPROPYLBENZENE	134.222		178.3	670.0	29.0		876	20		424
425	C10H14	1-METHYL-3-ISOPROPYLBENZENE	134.222		175.1	666.0	29.4		861	20	38,142	425
426	C10H14	1-METHYL-4-ISOPROPYLBENZENE	134.222	-73.2	177.1	653.0	28.3		857	20		426
427	C10H14	1:4-DIETHYLBENZENE	134.222	-42.2	183.7	657.9	28.1	0.480	862	20	39,398	427
428	C10H14	1:2:4:5-TETRAMETHYLBENZENE	134.222	78.8	196.8	675.0	29.4	0.480	838	81	45,552	428
429	C10H15N	N-BUTYLANILINE	149.236	-14.2	240.7	721.0	28.4	0.518	932	20	48,944	429
430	C10H18	CIS-DECALIN	138.254	-43.2	195.7	702.2	31.4		897	20	39,356	430
431	C10H18	TRANS-DECALIN	138.254	-30.4	187.2	690.0	31.4		870	20	38,519	431
432	C10H19N	CAPRYLONITRILE	153.269	-17.9	242.8	622.0	32.5		820	20		432
433	C10H20	N-BUTYLCYCLOHEXANE	140.270	-74.8	180.9	667.0	31.5		799	20	38,519	433
434	C10H20	ISOBUTYLCYCLOHEXANE	140.270		171.3	659.0	31.2		795	20		434
435	C10H20	SEC-BUTYLCYCLOHEXANE	140.270		179.3	669.0	26.7		813	20		435
436	C10H20	TERT-BUTYLCYCLOHEXANE	140.270	-41.2	171.5	659.0	26.6		813	20		436
437	C10H20	1-DECENE	140.270	-66.3	170.5	615.0	22.1	0.650	741	20	38,686	437
438	C10H20O	MENTHOL	156.269	42.8	216.3	694.0						438
439	C10H22	N-DECANE	142.286	-29.7	174.1	617.6	21.1	0.603	730	20	39,306	439
440	C10H22	3:3:5-TRIMETHYLHEPTANE	142.286		155.6	609.6	23.2				36,676	440
441	C10H22	2:2:3:3-TETRAMETHYLHEXANE	142.286		160.3	623.1	25.1				36,383	441
442	C10H22	2:2:5:5-TETRAMETHYLHEXANE	142.286		137.4	581.5	21.9				35,295	442
443	C10H22O	1-DECANOL	158.285	6.9	230.2	700.0	22.3	0.600	830	20	50,242	443
444	C11H10	1-METHYLNAPHTHALENE	142.201	-30.5	244.6	772.0	35.7	0.445	1020	20	46,055	444
445	C11H10	2-METHYLNAPHTHALENE	142.201	34.5	241.0	761.0	35.1	0.462	990	40	46,055	445
446	C11H14O2	BUTYL BENZOATE	178.232	-22.2	249.8	723.0	26.3	0.561	1006	20	48,986	446
447	C11H22	N-HEXYLCYCLOPENTANE	154.297		203.1	660.1	21.4				41,198	447
448	C11H22	1-UNDECENE	154.297	-49.2	192.6	637.0	20.0		751	20	40,905	448
449	C11H24	N-UNDECANE	156.313	-25.6	195.9	638.8	19.7	0.660	740	20	41,533	449
450	C12H8	ACENAPHTHALENE	152.196	95.0	270.0	796.9	32.2	0.487				450

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
401			-1.93	126.53	-28.998	72.934E-02	-4.363E-04	99.981E-09	16.1545	3521.08	-64.64	45	190	401
402	463.17	266.08	-2.05	126.78	-27.310	71.762E-02	-4.224E-04	95.417E-09	16.1135	3516.31	-64.23	45	190	402
403			-9.59	124.64	-6.942	63.346E-02	-3.326E-04	66.110E-09	16.2121	3670.22	-66.07	56	206	403
404	872.74	297.75	-13.94	117.02	-4.668	62.383E-02	-3.263E-04	63.765E-09	16.2190	3622.58	-64.59	51	198	404
405	437.52	268.27	-16.08	118.03	-19.590	67.240E-02	-3.692E-04	76.995E-09	16.2893	3614.19	-63.57	48	193	405
406	549.08	293.93	-193.43	47.35	-62.517	98.892E-02	-5.795E-04	12.912E-08	15.8567	3363.62	-65.21	40	186	406
407									15.8260	3346.12	-63.71	57	167	407
408	471.00	258.92	-103.58	112.75	-3.718	81.224E-02	-4.509E-04	97.050E-09	16.0118	3305.03	-67.61	35	175	408
409	525.56	272.12	-229.19	24.83	3.144	67.742E-02	-1.928E-04	-2.981E-08	15.9671	3291.45	-71.33	39	179	409
410			-241.37	24.53	-45.632	10.555E-01	-7.172E-04	19.866E-08	15.8017	3164.17	-61.66	24	163	410
411			-243.38	22.52	-60.311	11.045E-01	-7.712E-04	21.876E-08	15.7639	3084.08	-61.94	18	155	411
412			254.18	13.44	-54.106	10.948E-01	-7.746E-04	22.546E-08	15.7445	3052.17	-62.24	42	147	412
413			231.95	35.09	-67.269	11.262E-01	-7.988E-04	23.061E-08	15.8709	3341.62	-57.57	77	167	413
414			-237.39	34.33	-54.583	10.890E-01	-7.570E-04	21.420E-08	15.7280	3220.55	-59.31	55	167	414
415			-237.22	32.66	-54.583	10.890E-01	-7.570E-04	21.420E-08	15.7363	3167.42	-58.21	45	157	415
416			-242.12	34.04	-67.403	11.681E-01	-8.612E-04	25.736E-08	15.6488	3049.98	-57.13	40	140	416
417			-236.39	34.12	-54.918	10.911E-01	-7.603E-04	21.579E-08	15.8029	3269.07	-58.19	52	152	417
418	873.32	352.57	151.06	223.74	-68.802	84.992E-02	-6.506E-04	19.808E-08	16.1426	3992.01	-71.29	87	252	418
419			27.63	167.05					16.2805	4009.49	-64.98	92	227	419
420	563.84	296.01	-13.82	144.78	-22.990	79.340E-02	-4.396E-04	85.704E-09	16.0793	3633.40	-71.77	62	213	420
421			-21.56						15.9524	3512.47	-69.03	53	203	421
422	582.82	295.82	-17.46		-65.147	98.934E-02	-7.214E-04	21.520E-08	15.9999	3544.19	-68.10	52	203	422
423			-22.69		-86.001	11.020E-01	-8.746E-04	28.265E-08	15.9300	3462.28	-69.87	50	199	423
424									15.9809	3564.52	-70.00	57	208	424
425			-29.31		-48.759	90.644E-02	-6.054E-04	16.274E-08	15.9811	3543.79	-69.22	55	205	425
426									15.9424	3539.21	-70.10	56	207	426
427			-22.27	137.96	-37.417	86.709E-02	-5.560E-04	14.110E-08	16.1140	3657.22	-71.18	62	214	427
428			-45.30	119.53	15.265	65.188E-02	-2.879E-04	32.569E-09	16.3023	3850.91	-71.72	88	227	428
429	1111.10	341.28	-169.06		-34.068	91.440E-02	-5.560E-04	12.874E-08	16.3994	4079.72	-96.15	112	287	429
430			-182.42	85.87	-112.457	11.183E-01	-6.607E-04	14.369E-08	15.8312	3671.61	-69.74	95	222	430
431	702.27	339.66	-182.42	73.48	-97.670	10.446E-01	-5.476E-04	89.807E-09	15.7989	3610.66	-66.49	90	197	431
432														432
433	598.30	311.39	-213.32	56.48	-62.957	10.627E-01	-6.305E-04	14.001E-08	15.9116	3542.57	-72.32	59	212	433
434									15.8141	3437.99	-69.99	82	182	434
435									15.8670	3524.57	-70.78	87	197	435
436									15.7884	3457.85	-67.04	84	177	436
437	518.37	277.80	-124.22	121.12	-4.664	90.770E-02	-5.058E-04	10.953E-08	16.0129	3448.18	-76.09	83	187	437
438									19.0161	5539.90	-37.85	212	56	438
439	558.61	288.37	-249.83	33.24	-7.913	96.087E-02	-5.288E-04	11.309E-08	16.0114	3456.80	-78.67	57	203	439
440			-258.74	33.58	-70.372	12.322E-01	-8.646E-04	24.551E-08	15.7848	3305.20	-67.66	40	275	440
441					-58.833	12.313E-01	-8.834E-04	25.849E-08	15.7598	3371.05	-64.09	41	190	441
442					-62.341	12.447E-01	-8.956E-04	26.180E-08	15.8446	3172.92	-66.15	27	165	442
443	1481.80	380.00	-401.93	-104.25	14.570	89.472E-02	-3.921E-04	34.508E-09	15.9395	3389.43	-139.00	103	230	443
444	862.89	361.76	116.94	217.84	-64.820	93.868E-02	-6.942E-04	20.155E-08	16.2008	4206.70	-78.15	107	278	444
445	695.42	351.79	116.18	216.29	-56.518	89.974E-02	-6.469E-04	18.401E-08	16.2758	4237.37	-74.75	104	275	445
446	882.36	350.34			-17.367	86.751E-02	-4.610E-04	72.348E-09	16.3363	4158.47	-94.15	117	297	446
447	617.57	318.65	-209.63	78.25	-58.322	11.279E-01	-6.536E-04	14.729E-08	16.0140	3702.56	-81.55	78	234	447
448	566.26	294.89	-144.86	129.54	-5.585	10.027E-01	-5.602E-04	12.163E-08	16.0412	3597.72	-83.41	72	223	448
449	605.50	305.01	-270.47	41.62	-8.395	10.538E-01	-5.799E-04	12.368E-08	16.0541	3614.07	-85.45	75	225	449
450					-64.623	88.509E-02	-5.853E-04	13.054E-08	16.3091	4470.92	-81.40	177	377	450

NO	FORMULA	COMPOUND NAME	MOLWT	TFP	TBP	TC	PC	VC	LDEN	TDEN	HVAP	NO
451	C12H10	DIPHENYL	154.212	69.2	255.2	789.0	38.5	0.502	990	74	45,636	451
452	C12H10O	DIPHENYL ETHER	170.211	26.8	258.0	766.0	31.4		1066	30	47,143	452
453	C12H24	N-HEPTYLCYCLOPENTANE	168.324		224.1	679.0	19.5				43,375	453
454	C12H24	1-DODECENE	168.324	-35.2	213.3	657.0	18.5		758	20	42,998	454
455	C12H26	N-DODECANE	170.340	-9.6	216.3	658.3	18.2	0.713	748	20	43,668	455
456	C12H26O	DIHEXYL ETHER	186.339	-43.2	226.4	657.0	18.2	0.720	794	20	45,636	456
457	C12H26O	DODECANOL	186.339	23.9	259.9	679.0	19.3	0.718	835	20		457
458	C12H27N	TRIBUTYLAMINE	185.355		213.4	643.0	18.2		779	20	44,380	458
459	C13H10	FLUORENE	166.223	114.0	297.9	822.3	29.9	0.534				459
460	C13H12	DIPHENYLMETHANE	168.239	26.8	264.3	767.0	29.8		1006	20		460
461	C13H26	N-OCTYLCYCLOPENTANE	182.351		243.7	694.0	17.9				45,427	461
462	C13H26	1-TRIDECENE	182.351	-23.1	232.7	674.0	17.0		766	20	45,008	462
463	C13H28	N-TRIDECANE	184.367	-5.4	235.4	675.8	17.2	0.780	756	20	45,678	463
464	C14H10	ANTHRACENE	178.234	216.5	341.2	883.0					56,522	464
465	C14H10	PHENANTHRENE	178.234	100.5	339.4	878.0					55,684	465
466	C14H28	N-NONYLCYCLOPENTANE	196.378		262.1	710.5	16.5				47,269	466
467	C14H28	1-TETRADECENE	196.378	-12.9	251.1	689.0	15.6		786	0	46,934	467
468	C14H30	N-TETRADECANE	198.394	5.8	253.5	694.0	16.2	0.830	763	20	47,646	468
469	C15H12	1-PHENYLINDENE	192.261		322.0	843.7	27.0	0.598				469
470	C15H14	2-ETHYLFLUORENE	194.277		309.0	811.1	24.6	0.629				470
471	C15H30	N-DECYLCYCLOPENTANE	210.405		279.3	723.8	15.2				49,027	471
472	C15H30	1-PENTADECENE	210.405	-3.8	268.3	704.0	14.6		791	0	48,692	472
473	C15H32	N-PENTADECANE	212.421	9.8	270.6	707.0	15.2	0.880	769	20	49,488	473
474	C16H10	FLUORANTHENE	202.256	110.0	393.0	936.6	26.0	0.660				474
475	C16H10	PYRENE	202.256	151.0	362.0	892.1	26.0	0.637				475
476	C16H12	N-PHENYLNAPHTHALENE	204.272		316.0	840.1	26.3	0.605				476
477	C16H22O4	DIBUTYL-O-PHTHALATE	278.350	-35.2	334.8				1047	20	79,131	477
478	C16H32	N-DECYLCYCLOHEXANE	224.432		297.6	750.0	13.6				50,409	478
479	C16H32	1-HEXADECENE	224.432	4.1	284.8	717.0	13.4		788	10	50,451	479
480	C16H32O2	PALMIC ACID	256.431	63.0	348.5	791.0	19.0	0.946	828	102	66,992	480
481	C16H34	N-HEXADECANE	226.448	17.8	286.8	717.0	14.2		773	20	51,246	481
482	C17H34	N-DODECYLCYCLOPENTANE	238.459		310.9	750.0	13.0				52,628	482
483	C17H36O	HEPTADECANOL	256.474	53.8	323.8	736.0	14.2		848	54	60,709	483
484	C17H36	N-HEPTADECANE	240.475	21.8	302.0	733.0	13.2	1.000	778	20	52,921	484
485	C18H12	CHRYSENE	228.294	255.0	448.0	993.6	23.9	0.736				485
486	C18H14	O-TERPHENYL	230.310	56.8	331.8	891.0	39.0	0.769				486
487	C18H14	M-TERPHENYL	230.310	86.8	364.8	924.8	35.1	0.784				487
488	C18H14	P-TERPHENYL	230.310	211.8	375.8	926.0	33.2	0.779				488
489	C18H34O2	OLEIC ACID	282.469	13.3	362.3	797.0	17.0	1.035	893	20	68,131	489
490	C18H36	1-OCTADECENE	252.486	17.6	314.8	739.0	11.3		789	20	54,303	490
491	C18H36	N-TRIDECYLCYCLOPENTANE	252.486		325.4	761.0	12.1				54,345	491
492	C18H36O2	STEARIC ACID	284.485	70.0	371.9	810.0	16.5	1.054	844	70	70,049	492
493	C18H38	N-OCTADECANE	254.502	28.1	316.3	745.0	12.1		777	28	54,512	493
494	C18H38O	1-OCTADECANOL	270.501	57.8	334.8	747.0	14.2		812	59		494
495	C19H38	N-TETRADECYLCYCLOPENTANE	266.513		325.8	772.0	11.2				56,019	495
496	C19H40	N-NONADECANE	268.529	31.8	329.9	756.0	11.1		789	32	56,061	496
497	C20H40	N-PENTADECYLCYCLOPENTANE	280.540		351.8	780.0	10.2				57,694	497
498	C20H42	N-EICOSANE	282.556	36.8	343.8	767.0	11.1		775	40	57,527	498
499	C20H42O	1-EICOSANOL	298.555	65.8	355.8	770.0	12.2				65,314	499
500	C21H42	N-HEXADECYLCYCLOPENTANE	294.567		363.8	791.0	9.7				59,369	500

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CHEMICAL ENGINEERING

NO	VISA	VISB	DELHF	DELGF	CPVAPA	CPVAPB	CPVAPC	CPVAPD	ANTA	ANTB	ANTC	TMN	TMX	NO
451	733.87	369.58	182.21	280.26	-97.067	11.057E-01	-8.855E-04	27.901E-08	16.6832	4602.23	-70.42	70	272	451
452	1146.00	379.29	49.99		-60.730	92.821E-02	-5.870E-04	13.586E-08	16.3459	4310.25	-87.31	145	325	452
453	654.77	333.12	-230.27	86.67	-59.264	12.234E-01	-7.084E-04	15.964E-08	16.0589	3850.38	-88.75	95	256	453
454	615.67	310.07	-165.46	138.00	-6.544	10.978E-01	-6.155E-04	13.410E-08	16.0610	3729.87	-90.88	88	244	454
455	631.63	318.78	-291.07	50.07	-9.328	11.489E-01	-6.347E-04	13.590E-08	16.1134	3774.56	-91.31	91	247	455
456	723.43	323.35			33.536	10.735E-01	-5.535E-04	16.777E-08	16.3372	3982.78	-89.15	100	272	456
457	1417.80	398.89	-443.13	-87.13	9.224	11.032E-01	-5.338E-04	77.791E-09	15.2638	3242.04	-157.10	134	307	457
458	889.06	312.48			7.993	11.978E-01	-6.703E-04	14.486E-08	16.2878	3865.58	-86.15	89	258	458
459					-54.491	90.351E-02	-5.388E-04	92.570E-09	18.2166	6462.60	-13.40	207	407	459
460									14.4856	2902.44	-167.90	200	290	460
461	695.83	346.19	-250.87	95.12	-59.951	13.167E-01	-7.612E-04	17.082E-08	16.0941	3983.01	-95.85	112	276	461
462	658.16	323.71	-186.10	146.37	-7.118	11.911E-01	-6.674E-04	14.511E-08	16.0850	3856.23	-97.94	104	264	462
463	664.10	332.10	-311.71	58.49	-10.463	12.452E-01	-6.912E-04	14.897E-08	16.1355	3892.91	-98.93	107	267	463
464	513.28	405.81	224.83		-58.979	10.057E-01	-6.594E-04	16.056E-08	17.6701	6492.44	-26.13	217	382	464
465			202.64		-58.979	10.057E-01	-6.594E-04	16.056E-08	16.7187	5477.94	-69.39	177	382	465
466	735.19	357.74	-271.51	103.50	-60.809	14.118E-01	-8.156E-04	18.347E-08	16.1089	4096.30	-103.00	127	296	466
467	697.49	336.13	-206.66	154.87	-7.967	12.858E-01	-7.210E-04	15.692E-08	16.1643	4018.01	-102.70	119	284	467
468	689.85	344.21	-332.35	66.86	-10.982	13.377E-01	-7.423E-04	15.981E-08	16.1480	4008.52	-105.40	121	287	468
469					-96.154	11.865E-01	-7.786E-04	17.650E-08	16.4170	4872.90	-97.30	227	427	469
470					-107.036	12.611E-01	-8.156E-04	17.928E-08	16.5199	4789.44	-97.90	207	407	470
471	771.74	368.30	-292.15	111.91	-61.923	15.077E-01	-8.717E-04	19.590E-08	16.1261	4203.94	-109.70	140	313	471
472	739.13	347.46	-227.39	163.16	-9.203	13.825E-01	-7.783E-04	17.028E-08	16.1539	4103.15	-110.60	133	301	472
473	718.51	355.92	-352.99	75.28	-11.916	14.327E-01	-7.972E-04	17.199E-08	16.1724	4121.51	-111.80	135	304	473
474					-80.706	11.715E-01	-7.938E-04	18.600E-08	16.4523	5438.77	-112.40	287	487	474
475					-94.379	11.916E-01	-7.930E-04	17.559E-08	16.4842	5203.08	-107.20	257	477	475
476					-99.516	11.463E-01	-6.113E-04	60.612E-09	16.9691	5351.04	-81.70	227	427	476
477	2588.10	336.24			1.880	12.539E-01	-6.121E-04	69.710E-09	16.9539	4852.47	-138.10	196	384	477
478	925.84	378.69			-69.015	16.542E-01	-9.613E-04	21.428E-08	16.1627	4373.37	-111.80	190	300	478
479	767.48	357.85	-247.98	171.62	-9.705	14.750E-01	-8.298E-04	18.104E-08	16.2203	4245.00	-115.20	147	319	479
480			-723.06						18.9558	7049.18	-55.08	353	153	480
481	738.30	366.11	-373.59	83.74	-13.017	15.290E-01	-8.537E-04	18.497E-08	16.1841	4214.91	-118.70	150	321	481
482	853.53	385.53	-336.12	126.02	-63.263	16.952E-01	-9.768E-04	21.855E-08	16.1915	4395.87	-124.20	168	346	482
483			-546.25	-44.67	-7.792	16.529E-01	-9.345E-04	20.436E-08	15.6161	3672.62	-188.10	191	383	483
484	757.88	375.90	-394.19	92.15	-13.967	16.241E-01	-9.081E-04	19.720E-08	16.1510	4294.55	-124.00	161	337	484
485					-115.757	13.415E-01	-8.311E-04	15.412E-08	16.6038	5915.26	-128.10	377	577	485
486	1094.10	461.27												486
487	940.58	460.94												487
488	911.01	461.10												488
489			-646.02						18.2445	5884.49	-127.26	360	176	489
490	816.19	376.93	-289.22	188.45	-11.329	16.643E-01	-9.374E-04	20.486E-08	16.2221	4416.13	-127.30	171	350	490
491	891.80	392.78	-353.99	137.08	-64.209	17.903E-01	-1.032E-03	23.094E-08	16.2270	4483.13	-131.30	180	361	491
492			-764.51						19.8034	7709.35	-57.83	370	174	492
493	777.40	385.00	-414.83	100.57	-14.470	17.170E-01	-9.592E-04	20.783E-08	16.1232	4361.79	-129.90	172	352	493
494			-566.85	-36.22	-8.704	17.476E-01	-8.524E-04	21.575E-08	15.6898	3757.82	-193.10	201	385	494
495	924.60	399.62	-374.63	145.58	-64.929	18.845E-01	-1.085E-03	24.258E-08	16.2632	4439.38	-138.10	192	375	495
496	793.62	393.54	-435.43	108.98	-15.491	18.125E-01	-1.015E-03	22.052E-08	16.1533	4450.44	-135.60	183	366	496
497	950.57	406.33	-395.28	153.99	-66.093	19.804E-01	-1.140E-03	25.498E-08	16.3092	4642.01	-145.10	203	388	497
498	811.29	401.67	-456.07	117.40	-22.383	19.393E-01	-1.117E-03	25.284E-08	16.4685	4680.46	-141.10	198	379	498
499			-608.13	-19.43	-12.581	19.498E-01	-1.118E-03	25.158E-08	15.8233	3912.10	-203.10	219	406	499
500	977.42	412.29	-415.87	162.41	-66.683	20.741E-01	-1.237E-03	26.682E-08	16.3553	4715.69	-152.10	215	401	500

APPENDIX D

## *Conversion Factors for Some Common SI Units*

An asterisk (\*) denotes an exact relationship.

Length	*1 in.	:	25.4 mm
	*1 ft	:	0.3048 m
	*1 yd	:	0.9144 m
	1 mile	:	1.6093 km
	*1 Å(angstrom)	:	$10^{-10}$ m
Time	*1 min	:	60 s
	*1 h	:	3.6 ks
	*1 day	:	86.4 ks
	1 year	:	31.5 Ms
	*1 in. <sup>2</sup>	:	645.16 mm <sup>2</sup>
Area	1 ft <sup>2</sup>	:	0.092903 m <sup>2</sup>
	1 yd <sup>2</sup>	:	0.83613 m <sup>2</sup>
	1 acre	:	4046.9 m <sup>2</sup>
	1 mile <sup>2</sup>	:	2.590 km <sup>2</sup>
	Volume	1 in. <sup>3</sup>	:
1 ft <sup>3</sup>		:	0.02832 m <sup>3</sup>
1 yd <sup>3</sup>		:	0.76453 m <sup>3</sup>
1 UK gal		:	4546.1 cm <sup>3</sup>
1 US gal		:	3785.4 cm <sup>3</sup>
Mass	1 oz	:	28.352 g
	*1 lb	:	0.45359237 kg
	1 cwt	:	50.8023 kg
	1 ton	:	1016.06 kg
	Force	1 pdl	:
1 lbf		:	4.4482 N
1 kgf		:	9.8067 N
1 tonf		:	9.9640 kN
*1 dyn		:	$10^{-5}$ N
Temperature difference	*1 deg F (deg R)	:	$\frac{5}{9}$ deg C (deg K)
Energy (work, heat)	1 ft lbf	:	1.3558 J
	1 ft pdl	:	0.04214 J
	*1 cal (internat. table)	:	4.1868 J
	1 erg	:	$10^{-7}$ J
	1 Btu	:	1.05506 kJ
	1 hp h	:	2.6845 MJ
	*1 kW h	:	3.6 MJ
	1 therm	:	105.51 MJ
1 thermie	:	4.1855 MJ	
Calorific value (volumetric)	1 Btu/ft <sup>3</sup>	:	37.259 kJ/m <sup>3</sup>

Velocity	1 ft/s	:	0.3048 m/s
	1 mile/h	:	0.44704 m/s
Volumetric flow	1 ft <sup>3</sup> /s	:	0.028316 m <sup>3</sup> /s
	1 ft <sup>3</sup> /h	:	7.8658 cm <sup>3</sup> /s
	1 UK gal/h	:	1.2628 cm <sup>3</sup> /s
	1 US gal/h	:	1.0515 cm <sup>3</sup> /s
Mass flow	1 lb/h	:	0.12600 g/s
	1 ton/h	:	0.28224 kg/s
Mass per unit area	1 lb/in. <sup>2</sup>	:	703.07 kg/m <sup>2</sup>
	1 lb/ft <sup>2</sup>	:	4.8824 kg/m <sup>2</sup>
	1 ton/sq mile	:	392.30 kg/km <sup>2</sup>
Density	1 lb/in. <sup>3</sup>	:	27.680 g/cm <sup>3</sup>
	1 lb/ft <sup>3</sup>	:	16.019 kg/m <sup>3</sup>
	1 lb/UK gal	:	99.776 kg/m <sup>3</sup>
	1 lb/US gal	:	119.83 kg/m <sup>3</sup>
Pressure	1 lbf/in. <sup>2</sup>	:	6.8948 kN/m <sup>2</sup>
	1 tonf/in. <sup>2</sup>	:	15.444 MN/m <sup>2</sup>
	1 lbf/ft <sup>2</sup>	:	47.880 N/m <sup>2</sup>
	*1 standard atm	:	101.325 kN/m <sup>2</sup>
	*1 atm (1 kgf/cm <sup>2</sup> )	:	98.0665 kN/m <sup>2</sup>
	*1 bar	:	10 <sup>5</sup> N/m <sup>2</sup>
	1 ft water	:	2.9891 kN/m <sup>2</sup>
	1 in. water	:	249.09 N/m <sup>2</sup>
	1 in. Hg	:	3.3864 kN/m <sup>2</sup>
	1 mmHg (1 torr)	:	133.32 N/m <sup>2</sup>
Power (heat flow)	1 hp (British)	:	745.70 W
	1 hp (metric)	:	735.50 W
	1 erg/s	:	10 <sup>-7</sup> W
	1 ft lbf/s	:	1.3558 W
	1 Btu/h	:	0.29307 W
	1 ton of refrigeration	:	3516.9 W
Moment of inertia	1 lb ft <sup>2</sup>	:	0.042140 kg m <sup>2</sup>
Momentum	1 lb ft/s	:	0.13826 kg m/s
Angular momentum	1 lb ft <sup>2</sup> /s	:	0.042140 kg m <sup>2</sup> /s
Viscosity, dynamic	*1 P (Poise)	:	0.1 N* s/m <sup>2</sup>
	1 lb/ft h	:	0.41338 mN s/m <sup>2</sup>
	1 lb/ft s	:	1.4882 N s/m <sup>2</sup>
Viscosity, kinematic	*1 S (Stokes)	:	10 <sup>-4</sup> m <sup>2</sup> /s
	1 ft <sup>2</sup> /h	:	0.25806 cm <sup>2</sup> /s
Surface energy (surface tension)	1 erg/cm <sup>2</sup> (1 dyn/cm)	:	10 <sup>-3</sup> J/m <sup>2</sup> (10 <sup>-3</sup> N/m)
Mass flux density	1 lb/h ft <sup>2</sup>	:	1.3562 g/s m <sup>2</sup>
Heat flux density	1 Btu/h ft <sup>2</sup>	:	3.1546 W/m <sup>2</sup>
	*1 kcal/h m <sup>2</sup>	:	1.163 W/m <sup>2</sup>
Heat transfer coefficient	1 Btu/h ft <sup>2</sup> F	:	5.6783 W/m <sup>2</sup> K
Specific enthalpy (latent heat, etc.)	*1 Btu/lb	:	2.326 kJ/kg
Specific heat capacity	*1 Btu/lb °F	:	4.1868 kJ/kg K
Thermal conductivity	1 Btu/h ft °F 1 kcal/h m °C	:	1.7307 W/m K 1.163 W/m K

(Taken from MULLIN, J. W.: *The Chemical Engineer* No. 211 (Sept. 1967), 176.  
SI units in chemical engineering.)

*Note:* Where temperature difference is involved K = °C.

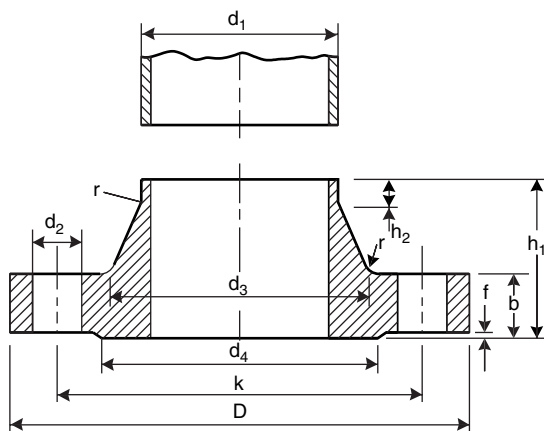


APPENDIX E

*Standard Flanges*

Steel welding-neck flanges for nominal pressure ratings of 6, 10, 25, 40 bar.

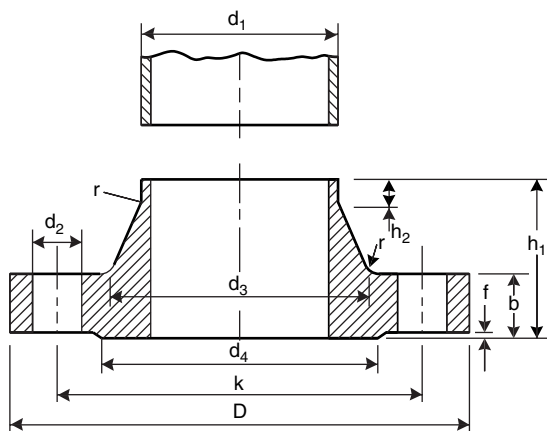
STEEL WELDING NECK FLANGES  
Nominal pressure 6 bar (1 bar = 10<sup>5</sup> N/m<sup>2</sup>)



Nom. size	Pipe o.d. $d_1$	Flange			Raised face		Bolting	Drilling			Neck		
		$D$	$b$	$h_1$	$d_4$	$f$		No.	$d_2$	$k$	$d_3$	$h_2 \approx$	$r$
10	17.2	75	12	28	35	2	M10	4	11	50	26	6	4
15	21.3	80	12	30	40	2	M10	4	11	55	30	6	4
20	26.9	90	14	32	50	2	M10	4	11	65	38	6	4
25	33.7	100	14	35	60	2	M10	4	11	75	42	6	4
32	42.4	120	14	35	70	2	M12	4	14	90	55	6	6
40	48.3	130	14	38	80	3	M12	4	14	100	62	7	6
50	60.3	140	14	38	90	3	M12	4	14	110	74	8	6
65	76.1	160	14	38	110	3	M12	4	14	130	88	9	6
80	88.9	190	16	42	128	3	M16	4	18	150	102	10	8
100	114.3	210	16	45	148	3	M16	4	18	170	130	10	8
125	139.7	240	18	48	178	3	M16	8	18	200	155	10	8
150	168.3	265	18	48	202	3	M16	8	18	225	184	12	10
200	219.1	320	20	55	258	3	M16	8	18	280	236	15	10
250	273	375	22	60	312	3	M16	12	18	335	290	15	12
300	323.9	440	22	62	365	4	M20	12	22	395	342	15	12
350	355.6	490	22	62	415	4	M20	12	22	445	385	15	12
400	406.4	540	22	65	465	4	M20	16	22	495	438	15	12
450	457.2	595	24	65	520	4	M20	16	22	550	492	15	12
500	508	645	24	68	570	4	M20	20	22	600	538	15	12
600	609.6	755	24	70	670	5	M24	20	26	705	640	16	12
700	711.2	860	24	70	775	5	M24	24	26	810	740	16	12
800	812.8	975	24	70	880	5	M27	24	30	920	842	16	12
900	914.4	1075	26	70	980	5	M27	24	30	1020	942	16	12
1000	1016	1175	26	70	1080	5	M27	28	30	1120	1045	16	16
1200	1220	1405	28	90	1295	5	M30	32	33	1340	1248	20	16
1400	1420	1630	32	90	1510	5	M33	36	36	1560	1452	20	16
1600	1620	1830	34	90	1710	5	M33	40	36	1760	1655	20	16
1800	1820	2045	36	100	1920	5	M36	44	39	1970	1855	20	16
2000	2020	2265	38	110	2125	5	M39	48	42	2180	2058	25	16

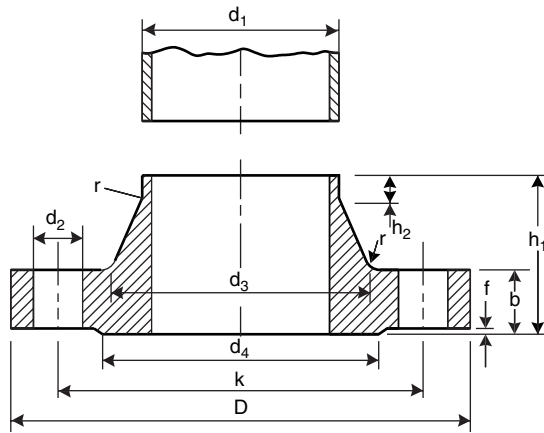


STEEL WELDING NECK FLANGES  
Nominal pressure 25 bar (1 bar =  $10^5$  N/m<sup>2</sup>)



Nom. size	Pipe o.d. $d_1$	Flange			Raised face		Bolting	Drilling			Neck		
		$D$	$b$	$h_1$	$d_4$	$f$		No.	$d_2$	$k$	$d_3$	$h_2$ $\approx$	$r$
175	193.7	330	28	75	248	3	M24	12	26	280	218	15	10
200	219.1	360	30	80	278	3	M24	12	26	310	244	16	10
250	273	425	32	88	335	3	M27	12	30	370	298	18	12
300	323.9	485	34	92	395	4	M27	16	30	430	352	18	12
350	355.6	555	38	100	450	4	M30	16	33	490	398	20	12
400	406.4	620	40	110	505	4	M33	16	36	550	452	20	12
450	457.2	670	42	110	555	4	M33	20	36	600	505	20	12
500	508	730	44	125	615	4	M33	20	36	660	558	20	12
600	609.6	845	46	125	720	5	M36	20	39	770	660	20	12
700	711.2	960	46	125	820	5	M39	24	42	875	760	20	12
800	812.8	1085	50	135	930	5	M45	24	48	990	865	22	12
900	914.4	1185	54	145	1030	5	M45	28	48	1090	968	24	12
1000	1016	1320	58	155	1140	5	M52	28	56	1210	1070	24	16

STEEL WELDING NECK FLANGES  
Nominal pressure 40 bar (1 bar =  $10^5$  N/m<sup>2</sup>)



Nom. size	Pipe o.d. $d_1$	Flange			Raised face		Bolting	Drilling			Neck		
		$D$	$b$	$h_1$	$d_4$	$f$		No.	$d_2$	$k$	$d_3$	$h_2$ $\approx$	$r$
10	17.2	90	16	35	40	2	M12	4	14	60	28	6	4
15	21.3	95	16	38	45	2	M12	4	14	65	32	6	4
20	26.9	105	18	40	58	2	M12	4	14	75	40	6	4
25	33.7	115	18	40	68	2	M12	4	14	85	46	6	4
32	42.4	140	18	42	78	2	M16	4	18	100	56	6	6
40	48.3	150	18	45	88	3	M16	4	18	110	64	7	6
50	60.3	165	20	48	102	3	M16	4	18	125	75	8	6
65	76.1	185	22	52	122	3	M16	8	18	145	90	10	6
80	88.9	200	24	58	138	3	M16	8	18	160	105	12	8
100	114.3	235	24	65	162	3	M20	8	22	190	134	12	8
125	139.7	270	26	68	188	3	M24	8	26	220	162	12	8
150	168.3	300	28	75	218	3	M24	8	26	250	192	12	10
175	193.7	350	32	82	260	3	M27	12	30	295	218	15	10
200	219.1	375	34	88	285	3	M27	12	30	320	244	16	10
250	273	450	38	105	345	3	M30	12	33	385	306	18	12
300	323.9	515	42	115	410	4	M30	16	33	450	362	18	12
350	355.6	580	46	125	465	4	M33	16	36	510	408	20	12
400	406.4	660	50	135	535	4	M36	16	39	585	462	20	12
450	457.2	685	50	135	560	4	M36	20	39	610	500	20	12
500	508	755	52	140	615	4	M39	20	42	670	562	20	12

## APPENDIX F

# *Design Projects*

EIGHT typical design exercises are given in this appendix. They have been adapted from Design Projects set by the Institution of Chemical Engineers as the final part of the Institution's qualifying examinations for professional Chemical Engineers.

### **F.1 ETHYLHEXANOL FROM PROPYLENE AND SYNTHESIS GAS**

#### **The project**

Design a plant to produce 40,000 tonnes/year of 2-ethylhexanol from propylene and synthesis gas, assuming an operating period of 8000 hours on stream.

#### ***The process***

The first stage of the process is a hydroformylation (oxo) reaction from which the main product is n-butyraldehyde. The feeds to this reactor are synthesis gas (CO/H<sub>2</sub> mixture) and propylene in the molar ratio 2 : 1, and the recycled products of isobutyraldehyde cracking. The reactor operates at 130°C and 350 bar, using cobalt carbonyl as catalyst in solution. The main reaction products are n- and isobutyraldehyde in the ratio of 4 : 1, the former being the required product for subsequent conversion to 2-ethylhexanol. In addition, 3 per cent of the propylene feed is converted to propane whilst some does not react.

Within the reactor, however, 6 per cent of the n-butyraldehyde product is reduced to n-butanol, 4 per cent of the isobutyraldehyde product is reduced to isobutanol, and other reactions occur to a small extent yielding high molecular weight compounds (heavy ends) to the extent of 1 per cent by weight of the butyraldehyde/butanol mixture at the reactor exit.

The reactor is followed by a gas-liquid separator operating at 30 bar from which the liquid phase is heated with steam to decompose the catalyst for recovery of cobalt by filtration. A second gas-liquid separator operating at atmospheric pressure subsequently yields a liquid phase of aldehydes, alcohols, heavy ends and water, which is free from propane, propylene, carbon monoxide and hydrogen.

This mixture then passes to a distillation column which gives a top product of mixed butyraldehydes, followed by a second column which separates the two butyraldehydes into an isobutyraldehyde stream containing 1.3 per cent mole n-butyraldehyde and an n-butyraldehyde stream containing 1.2 per cent mole isobutyraldehyde.

A cracker converts isobutyraldehyde at a pass yield of 80 per cent back to propylene, carbon monoxide and hydrogen by passage over a catalyst with steam. After separation of the water and unreacted isobutyraldehyde the cracked gas is recycled to the hydroformylation reactor. The isobutyraldehyde is recycled to the cracker inlet. The operating conditions of the cracker are 275°C and 1 bar.

The n-butyraldehyde is treated with a 2 per cent w/w aqueous sodium hydroxide and undergoes an aldol condensation at a conversion efficiency of 90 per cent. The product of this reaction, 2-ethylhexanal, is separated and then reduced to 2-ethylhexanol by hydrogen in the presence of a Raney nickel catalyst with a 99 per cent conversion rate. In subsequent stages of the process (details of which are not required), 99.8 per cent of the 2-ethylhexanol is recovered at a purity of 99 per cent by weight.

### **Feed specifications**

- (i) Propylene feed: 93 per cent propylene, balance propane.
- (ii) Synthesis gas: from heavy fuel oil, after removal of sulphur compounds and carbon dioxide:  
H<sub>2</sub> 48.6 per cent; CO 49.5 per cent; CH<sub>4</sub> 0.4 per cent; N<sub>2</sub> 1.5 per cent.

### **Utilities**

- (i) Dry saturated steam at 35 bar.
- (ii) Cooling water at 20°C.
- (iii) 2 per cent w/w aqueous sodium hydroxide solution.
- (iv) Hydrogen gas: H<sub>2</sub> 98.8 per cent; CH<sub>4</sub> 1.2 per cent.

## **Scope of design work required**

### **1. Process design**

- (a) Prepare a material balance for the complete process.
- (b) Prepare a process diagram for the plant showing the major items of equipment. Indicate the materials of construction and the operating temperatures and pressures.
- (c) Prepare energy balances for the hydroformylation reactor and for the isobutyraldehyde cracking reactor.

### **2. Chemical engineering design**

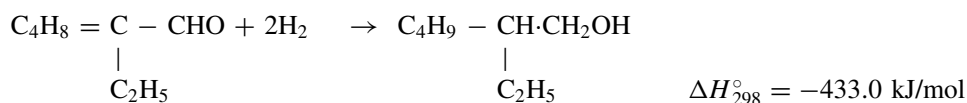
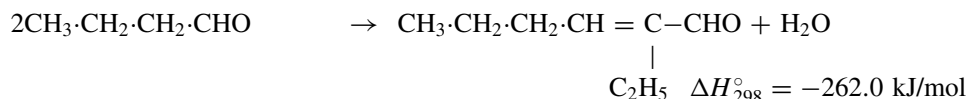
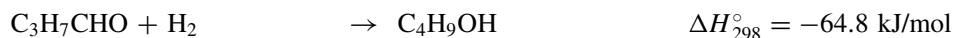
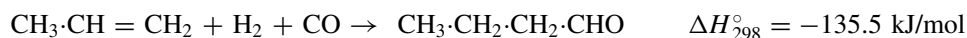
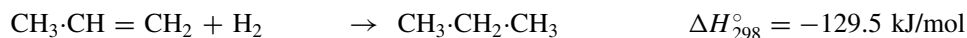
Prepare a chemical engineering design of the second distillation unit, i.e. for the separation of n- and isobutyraldehyde. Make dimensioned sketches of the column, the reboiler and the condenser.

### **3. Mechanical design**

Prepare a mechanical design with sketches suitable for submission to a drawing office of the n- and isobutyraldehyde distillation column.

### **4. Control system**

For the hydroformylation reactor prepare a control scheme to ensure safe operation.

**Data****1. Reactions****2. Boiling points at 1 bar**

Propylene	-47.7°C
Propane	-42.1°C
n-Butyraldehyde	75.5°C
Isobutyraldehyde	64.5°C
n-Butanol	117.0°C
Isobutanol	108.0°C
2-Ethylhexanol	184.7°C

**3. Solubilities of gases at 30 bar in the liquid phase of the first gas-liquid separator**

H <sub>2</sub>	0.08 × 10 <sup>-3</sup>	kg dissolved/kg liquid
CO	0.53 × 10 <sup>-3</sup>	kg dissolved/kg liquid
Propylene	7.5 × 10 <sup>-3</sup>	kg dissolved/kg liquid
Propane	7.5 × 10 <sup>-3</sup>	kg dissolved/kg liquid

**4. Vapour-liquid equilibrium of the butyraldehydes at 1 atm (Ref. 7)**

T°C	x	y
73.94	0.1	0.138
72.69	0.2	0.264
71.40	0.3	0.381
70.24	0.4	0.490
69.04	0.5	0.589
68.08	0.6	0.686
67.07	0.7	0.773
65.96	0.8	0.846
64.95	0.9	0.927



where  $x$  and  $y$  are the mol fractions of the more volatile component (isobutyraldehyde) in the liquid and vapour phases respectively.

## REFERENCES

1. *Propylene and its Industrial Derivatives*, HANCOCK, E. G. (ed.), John Wiley & Sons N. Y., 1973, Chapter 9, pp. 333–367.
2. *Carbon Monoxide in Organic Synthesis*. Falbe-Springer Verlag, New York, 1970, pp. 1–75.
3. *Chemical Engineering*, **81**, Sept. 30th, 1974, pp. 115–122. Physical and thermodynamic properties of CO and CO<sub>2</sub>.
4. *Chemical Engineering*, **82**, Jan. 20th, 1975, pp. 99–106. Physical and thermodynamic properties of H<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub>.
5. *Chemical Engineering*, **82**, Mar. 31st, 1975, pp. 101–109. Physical and thermodynamic properties of C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/iC<sub>4</sub>H<sub>8</sub>.
6. *Chemical Engineering*, **82**, May 12th, 1975, pp. 89–97. Physical and thermodynamic properties of CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>.
7. J. G. WOJTASINSKI. *J. Chem. Eng. Data*, 1963 (July), pp. 381–385. Measurement of total pressures for determining liquid-vapour equilibrium relations of the binary system isobutyraldehyde-n-butyraldehyde.
8. H. WEBER and J. FALBE. *Ind. Eng. Chem.* 1970 (April), pp. 33–7. Oxo Synthesis Technology.
9. *Hydrocarbon Processing*, Nov. 1971, p. 166.
10. *Hydrocarbon Processing*, Nov. 1975, p. 148.

## F.2 CHLOROBENZENES FROM BENZENE AND CHLORINE

### The project

Design a plant to produce 20,000 tonnes/year of monochlorobenzene together with not less than 2000 tonnes/year of dichlorobenzene, by the direct chlorination of benzene.

### The process

Liquid benzene (which must contain less than 30 ppm by weight of water) is fed into a reactor system consisting of two continuous stirred tanks operating in series at 2.4 bar. Gaseous chlorine is fed in parallel to both tanks. Ferric chloride acts as a catalyst, and is produced *in situ* by the action of hydrogen chloride on mild steel. Cooling is required to maintain the operating temperature at 328 K. The hydrogen chloride gas leaving the reactors is first cooled to condense most of the organic impurities. It then passes to an activated carbon adsorber where the final traces of impurity are removed before it leaves the plant for use elsewhere.

The crude liquid chlorobenzenes stream leaving the second reactor is washed with water and caustic soda solution to remove all dissolved hydrogen chloride. The product recovery system consists of two distillation columns in series. In the first column (the “benzene column”) unreacted benzene is recovered as top product and recycled. In the second column (the “chlorobenzene column”) the mono- and dichlorobenzenes are separated. The recovered benzene from the first column is mixed with the raw benzene feed and this combined stream is fed to a distillation column (the “drying column”) where water is removed as overhead. The benzene stream from the bottom of the drying column is fed to the reaction system.

**Feed specifications**

- (i) Chlorine: 293 K, atmospheric pressure, 100 per cent purity.
- (ii) Benzene: 293 K, atmospheric pressure, 99.95 wt per cent benzene, 0.05 wt per cent water.

**Product specifications**

- (i) Monochlorobenzene: 99.7 wt per cent.
- (ii) Dichlorobenzene: 99.6 wt per cent.
- (iii) Hydrogen chloride gas: less than 250 ppm by weight benzene.

**Utilities**

- (i) Stream: dry saturated at 8 bar and at 28 bar.
- (ii) Cooling water: 293 K.
- (iii) Process water: 293 K.
- (iv) Caustic soda solution: 5 wt per cent NaOH, 293 K.
- (v) Electricity: 440 V, 50 Hz, 3 phase.

**Scope of design work required****1. Process design**

- (a) Prepare a materials balance for the process including an analysis of each reactor stage (the kinetics of the chlorination reactions are given below). Onstream time may be taken as 330 days per year.
- (b) Prepare energy balances for the first reactor and for the chlorobenzene column (take the reflux ratio for this column as twice the minimum reflux ratio).
- (c) Prepare a process flow diagram for the plant. This should show the major items of equipment with an indication of the materials of construction and of the internal layout. Temperatures and pressures should also be indicated.

**2. Chemical engineering design**

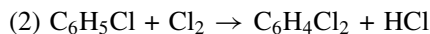
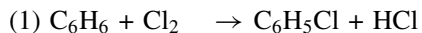
Prepare a sieve-plate column design for the chlorobenzene distillation and make dimensioned sketches showing details of the plate layout including the weir and the downcomer.

**3. Mechanical design**

Prepare a mechanical design of the chlorobenzene column, estimating the shell thickness, the positions and sizes of all nozzles, and the method of support for the plates and the column shell. Make a dimensioned sketch suitable for submission to a drawing office.

**4. Safety**

Indicate the safety measures required for this plant bearing in mind the toxic and inflammable materials handled.

**Data****1. The reactions**

The dichlorobenzene may be assumed to consist entirely of the para-isomer and the formation of trichlorobenzenes may be neglected.

The rate equations can be written in first-order form when the concentration of dissolved chlorine remains essentially constant. Thus:

$$r_B = -k_1 x_B$$

$$r_M = k_1 x_B - k_2 x_M$$

$$r_D = k_2 x_M$$

where  $r$  is the reaction rate,

$k_1$  is the rate constant for reaction (1) at 328 K =  $1.00 \times 10^{-4} \text{s}^{-1}$ ,

$k_2$  is the rate constant for reaction (2) at 328 K =  $0.15 \times 10^{-4} \text{s}^{-1}$

and  $x$  denotes mol fraction.

The subscripts B, M and D denote benzene, monochlorobenzene and dichlorobenzene respectively.

Yields for the reactor system should be calculated on the basis of equal liquid residence times in the two reactors, with a negligible amount of unreacted chlorine in the vapour product streams. It may be assumed that the liquid product stream contains 1.5 wt per cent of hydrogen chloride:

Reference: BODMAN, SAMUEL W. *The Industrial Practice of Chemical Process Engineering*, 1968, The MIT Press.

**2. Solubilities**

Solubility of the water/benzene system (taken from Seidell, A. S., *Solubilities of Organic Compounds*, 3rd edn, Vol. II, 1941, Van Nostrand).

Temperature (K)	293	303	313	323
g H <sub>2</sub> O/100 g C <sub>6</sub> H <sub>6</sub>	0.050	0.072	0.102	0.147
g C <sub>6</sub> H <sub>6</sub> /100 g H <sub>2</sub> O	0.175	0.190	0.206	0.225

**3. Thermodynamic and physical properties**

	C <sub>6</sub> H <sub>6</sub> liquid	C <sub>6</sub> H <sub>6</sub> gas	C <sub>6</sub> H <sub>5</sub> Cl liquid	C <sub>6</sub> H <sub>5</sub> Cl gas	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> liquid	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> gas
Heat of formation at 298 K (kJ/kmol)	49.0	82.9	7.5	46.1	-42.0	5.0
Heat capacity (kJ/kmol K)						
298 K	136	82	152	92		103
350 K	148	99	161	108	193	118
400 K	163	113	170	121	238	131
450 K	179	126	181	134	296	143
500 K	200	137	192	145	366	155

		C <sub>6</sub> H <sub>6</sub> liquid	C <sub>6</sub> H <sub>6</sub> gas	C <sub>6</sub> H <sub>5</sub> Cl liquid	C <sub>6</sub> H <sub>5</sub> Cl gas	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> liquid	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> gas
Density (kg/m <sup>3</sup> )	298 K	872		1100			
	350 K	815		1040		1230	
	400 K	761		989		1170	
	450 K	693		932		1100	
	500 K	612		875		1020	
Viscosity (Ns/m <sup>2</sup> )	298 K	0.598 × 10 <sup>-3</sup>		0.750 × 10 <sup>-3</sup>			
	350 K	0.326 × 10 <sup>-3</sup>		0.435 × 10 <sup>-3</sup>		0.697 × 10 <sup>-3</sup>	
	400 K	0.207 × 10 <sup>-3</sup>		0.305 × 10 <sup>-3</sup>		0.476 × 10 <sup>-3</sup>	
	450 K	0.134 × 10 <sup>-3</sup>		0.228 × 10 <sup>-3</sup>		0.335 × 10 <sup>-3</sup>	
	500 K	0.095 × 10 <sup>-3</sup>		0.158 × 10 <sup>-3</sup>		0.236 × 10 <sup>-3</sup>	
Surface tension (N/m)	298 K	0.0280		0.0314			
	350 K	0.0220		0.0276		0.0304	
	400 K	0.0162		0.0232		0.0259	
	450 K	0.0104		0.0177		0.0205	
	500 K	0.0047		0.0115		0.0142	

## REFERENCES

1. PERRY, R. H. and CHILTON, C. H. *Chemical Engineers' Handbook*, 5th edn, 1973, McGraw-Hill.
2. KIRK-OTHMER, *Encyclopaedia of Chemical Technology*, 2nd edn, 1964, John Wiley & Sons.

### F.3 METHYL ETHYL KETONE FROM BUTYL ALCOHOL

#### The project

Design a plant to produce  $1 \times 10^7$  kg/year of methyl ethyl ketone (MEK).

Feedstock: Secondary butyl alcohol.

Services available:

Dry saturated steam at 140°C.

Cooling water at 24°C.

Electricity at 440 V three-phase 50 Hz.

Flue gases at 540°C.

#### The process

The butyl alcohol is pumped from storage to a steam-heated preheater and then to a vaporiser heated by the reaction products. The vapour leaving the vaporiser is heated to its reaction temperature by flue gases which have previously been used as reactor heating medium. The superheated butyl alcohol is fed to the reaction system at 400°C to 500°C where 90 per cent is converted on a zinc oxide-brass catalyst to methyl ethyl ketone, hydrogen and other reaction products. The reaction products may be treated in one of the following ways:

- (a) Cool and condense the MEK in the reaction products and use the exhaust gases as a furnace fuel.
- (b) Cool the reaction products to a suitable temperature and separate the MEK by absorption in aqueous ethanol. The hydrogen off gas is dried and used as a furnace

fuel. The liquors leaving the absorbers are passed to a solvent extraction column, where the MEK is recovered using trichlorethane. The raffinate from this column is returned to the absorber and the extract is passed to a distillation unit where the MEK is recovered. The trichlorethane is recycled to the extraction plant.

### Scope of design work required

1. Prepare material balances for the two processes.
2. On the basis of the cost data supplied below decide which is the preferable process.
3. Prepare a material flow diagram of the preferred process.
4. Prepare a heat balance diagram of the preheater–vaporiser–superheater–reactor system.
5. Prepare a chemical engineering design of the preheater–vaporiser–superheater–reactor system and indicate the type of instrumentation required.
6. Prepare a mechanical design of the butyl alcohol vaporiser and make a dimensioned sketch suitable for submission to a drawing office.

### Data

#### *Process data*

Outlet condenser temperature = 32°C.

Vapour and liquid are in equilibrium at the condenser outlet.

Calorific value of MEK = 41,800 kJ/kg.

#### *Cost data*

Selling price of MEK	=	£9.60 per 100kg
Steam raising cost	=	£0.53 per 10 <sup>6</sup> kJ
Cost of tower shell	=	£2000
Cost of plates	=	£2000
Cost of reboiler	=	£2500
Cost of heat exchanger (per distillation column)	=	£8000
Cost of solvent extraction auxiliaries	=	£1000
Cost of absorption and distillation column packing, supports and distributors	=	£2000
Cost of tanks (surge, etc.)	=	£1000
Cost of control of whole plant	=	£9000
Cost of instrumentation for control of recovery section	=	£4500
Cost of electricity for pumps	=	£5000
Pump costs (total)	=	£3000
Cost of cooling water for whole plant	=	£5000

#### *Reactor data*

The “short-cut” method proposed in Ref. 1 may be used only to obtain a preliminary estimate of the height of catalyst required in the reactor. The reactor should be designed

from first principles using the rate equation, below, taken from Ref. 1.

$$r_A = \frac{C(P_{A,i} - P_{K,i}P_{H,i}/K)}{P_{K,i}(1 + K_A P_{A,i} + K_{AK} P_{A,i}/P_{K,i})}$$

where  $P_{A,i}$ ,  $P_{H,i}$ , and  $P_{K,i}$  are the interfacial partial pressures of the alcohol, hydrogen and ketone in bars, and the remaining quantities are as specified by the semi-empirical equations below:

$$\log_{10} C = -\frac{5964}{T_i} + 8.464$$

$$\log_{10} K_A = -\frac{3425}{T_i} + 5.231$$

$$\log_{10} K_{AK} = +\frac{486}{T_i} - 0.1968$$

In these equations, the interfacial temperature  $T_i$  is in Kelvin, the constant  $C$  is in  $\text{kmol/m}^2\text{h}$ ,  $K_A$  is in  $\text{bar}^{-1}$ , and  $K_{AK}$  is dimensionless.

The equilibrium constant,  $K$  is given in Ref. 1 (although the original source is Ref. 2) by the equation:

$$\log_{10} K = -\frac{2790}{T_i} + 1.510 \log_{10} T_i + 1.871$$

where  $K$  is in bar.

Useful general information will be found in Ref. 3.

## REFERENCES

1. PERONA, J. J. and THODOS, G. *AIChE JI*, 1957, **3**, 230.
2. KOLB, H. J. and BURWELL, R. L. (Jr.) *J. Am. Chem. Soc.*, 1945, **67**, 1084.
3. RUDD, D. F. and WATSON, C. C. *Strategy of Process Engineering*, 1968 (New York: John Wiley & Sons Inc.).

## F.4 ACRYLONITRILE FROM PROPYLENE AND AMMONIA

### The project

Design a plant to produce  $1 \times 10^8$  kg/year of acrylonitrile ( $\text{CH}_2:\text{CH}:\text{CN}$ ) from propylene and ammonia by the ammoxidation process.

Feedstock:

Ammonia: 100 per cent  $\text{NH}_3$ .

Propylene: Commercial grade containing 90 per cent  $\text{C}_3\text{H}_6$ , 10 per cent paraffins, etc., which do not take any part in the reaction.

Services available:

Dry saturated steam at  $140^\circ\text{C}$ .

Cooling water at  $24^\circ\text{C}$ .

Other normal services.

### **The process**

Propylene, ammonia, steam and air are fed to a vapour-phase catalytic reactor (item A). The feedstream composition (molar per cent) is propylene 7; ammonia 8; steam 20; air 65. A fixed-bed reactor is employed using a molybdenum-based catalyst at a temperature of 450°C, a pressure of 3 bar absolute, and a residence time of 4 seconds. Based upon a pure propylene feed, the carbon distribution by weight in the product from the reactor is:

Acrylonitrile	58 per cent
Acetonitrile	2 per cent
Carbon dioxide	16 per cent
Hydrogen cyanide	6 per cent
Acrolein	2 per cent
Unreacted propylene	15 per cent
Other by products	1 per cent

The reactor exit gas is air-cooled to 200°C and then passes to a quench scrubber (B) through which an aqueous solution containing ammonium sulphate 30 wt per cent and sulphuric acid 1 wt per cent is circulated. The exit gas temperature is thereby reduced to 90°C.

From the quench scrubber (B) the gas passes to an absorption column (C) in which the acrylonitrile is absorbed in water to produce a 3 wt per cent solution. The carbon dioxide, unreacted propylene, oxygen, nitrogen and unreacted hydrocarbons are not absorbed and are vented to atmosphere from the top of column (C).

The solution from the absorber (C) passes to a stripping column (D) where acrylonitrile and lower boiling impurities are separated from water. Most of the aqueous bottom product from the stripping column (D), which is essentially free of organics, is returned to the absorber (C), the excess being bled off. The overhead product is condensed and the aqueous lower layer returned to the stripping column (D) as reflux.

The upper layer which contains, in addition to acrylonitrile, hydrogen cyanide, acrolein, acetonitrile, and small quantities of other impurities, passes to a second reactor (E) where, at a suitable pH, all the acrolein is converted to its cyanohydrin. (Cyanohydrins are sometimes known as cyanhydrins.) The product from the reactor (E) is fed to a cyanohydrin separation column (F), operating at reduced temperature and pressure, in which acrolein cyanohydrin is separated as the bottom product and returned to the ammoxidation reactor (A) where it is quantitatively converted to acrylonitrile and hydrogen cyanide.

The top product from column (F) is fed to a stripping column (G) from which hydrogen cyanide is removed overhead.

The bottom product from column (G) passes to the hydroextractive distillation column (H). The water feed rate to column (H) is five times that of the bottom product flow from column (G). It may be assumed that the acetonitrile and other by-products are discharged as bottom product from column (H) and discarded. The overhead product from column (H), consisting of the acrylonitrile water azeotrope, is condensed and passed to a separator. The lower aqueous layer is returned to column (H).

The upper layer from the separator is rectified in a column (I) to give 99.95 wt per cent pure acrylonitrile.

## Scope of design work required

1. Prepare a material balance for the process.
2. Prepare a material flow diagram of the process.
3. Prepare a heat balance for the reactor (A) and quench column (B).
4. Prepare a chemical engineering design of reactor (A) and either column (B) OR column (D).
5. Prepare a mechanical design of the condenser for stripping column (D) and make a dimensioned sketch suitable for submission to a drawing office.
6. Indicate the instrumentation and safety procedure required for this plant bearing in mind the toxic and inflammable materials being handled.

## REFERENCES

1. HANCOCK, E. H. (ed.) *Propylene and its Industrial Derivatives*, 1973 (London: Ernest Benn Ltd.).
2. SOKOLOV, N. M., SEVRYUGOVA, N. N. and ZHAVORONKOV, N. M. *Proceedings of the International Symposium on Distillation*, 1969, pages 3 : 110-3 : 117 (London: I Chem E).

## F.5 UREA FROM AMMONIA AND CARBON DIOXIDE

### The project

A plant is to be designed for the production of 300,000 kg per day of urea by the reaction of ammonia and carbon dioxide at elevated temperature and pressure, using a total-recycle process in which the mixture leaving the reactor is stripped by the carbon dioxide feed (DSM process, references 1 to 4).

### Materials available

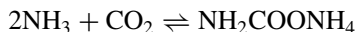
- (1) Liquid ammonia at 20°C and 9 bar, which may be taken to be 100 per cent pure.
- (2) Gaseous carbon dioxide at 20°C and atmospheric pressure, also 100 per cent pure.

All normal services are available on site. In particular, electricity, 440-V three-phase 50 Hz; cooling water at a maximum summer temperature of 22°C; steam at 40 bar with 20°C of superheat.

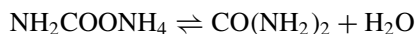
The on-stream time is to be 330 days/year, and the product specification is fertiliser-grade urea prills containing not more than 1.0 per cent biuret.

### The process

The reaction which produces urea from ammonia and carbon dioxide takes place in two stages; in the first, ammonium carbamate is formed:



In the second, the carbamate is dehydrated to give urea:





Both reactions are reversible, the first being exothermal and going almost to completion, whilst the second is endothermal and goes to 40 to 70 per cent of completion.

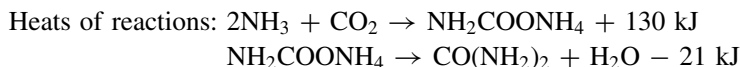
Ammonia and carbon dioxide are fed to the reactor, a stainless steel vessel with a series of trays to assist mixing. The reactor pressure is 125 bar and the temperature is 185°C.

The reactor residence time is about 45 minutes, a 95 per cent approach to equilibrium being achieved in this time. The ammonia is fed directly to the reactor, but the carbon dioxide is fed to the reactor upwardly through a stripper, down which flows the product stream from the reactor. The carbon dioxide decomposes some of the carbamate in the product stream, and takes ammonia and water to a high-pressure condenser. The stripper is steam heated and operates at 180°C, whilst the high-pressure condenser is at 170°C and the heat released in it by recombination of ammonia and carbon dioxide to carbamate is used to raise steam. Additional recycled carbamate solution is added to the stream in the high-pressure condenser, and the combined flow goes to the reactor.

The product stream leaving the stripper goes through an expansion valve to the low-pressure section, the operating pressure there being 5 bar. In a steam-heated rectifier, further ammonia and carbon dioxide are removed and, with some water vapour, are condensed to give a weak carbamate solution. This is pumped back to the high-pressure condenser.

A two-stage evaporative concentration under vacuum, with a limited residence-time in the evaporator to limit biuret formation, produces a urea stream containing about 0.5 per cent water which can be sprayed into a prilling tower.

### ***Physico-chemical data***



Properties of urea:

Density at 20°C = 1.335 g/cm<sup>3</sup>

Heat of solution in water = -250 J/g

Melting point = 133°C

Specific heat = 1.34 J/g at 20°C

### ***Reactor and stripper design***

The relationships between temperature, pressure, and composition for the Urea—CO<sub>2</sub>—NH<sub>3</sub>—H<sub>2</sub>O system are given in References 5 and 6. These are equilibrium relationships. The reaction velocity may be obtained from the graph in Figure 5 of Reference 5, which is reproduced below for ease of reference (Figure F1). Some stripper design data appear in Reference 7.

### **Scope of design work required**

1. Prepare a mass balance diagram for the process, on a weight per hour basis, through to the production of urea prills.
2. Prepare an energy balance diagram for the reactor–stripper–high-pressure condenser complex.

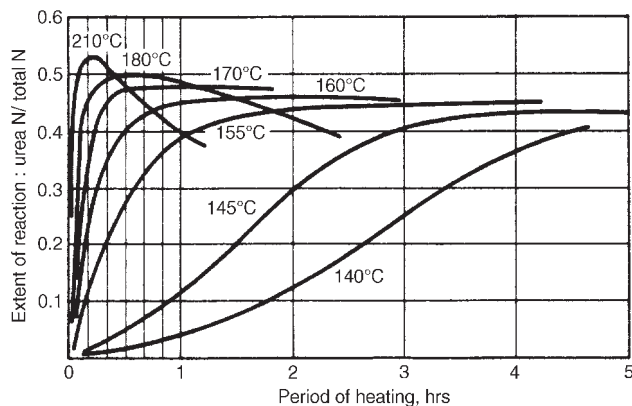


Figure F1. Rate of dehydration of carbamate

3. Prepare a process flow diagram, showing the major items of equipment in the correct elevation, with an indication of their internal construction. Show all major pipe lines and give a schematic outline of the probable instrumentation of the reactor and its subsidiaries.
4. Prepare an equipment schedule, listing the main plant items with their size, throughput, operating conditions, materials of construction, and services required.
5. Prepare an outline design of the reactor and carry out the chemical engineering design of the stripper, specifying the interfacial contact area which will need to be provided between the carbon dioxide stream and the product stream to enable the necessary mass transfer to take place.
6. Prepare a mechanical design of the stripper, which is a vertical steam-heated tube-bundle rather like a heat exchanger. Show how liquid is to be distributed to the tubes, and how the shell is to be constructed to resist the high pressure and the corrosive process material.
7. Prepare a detailed mechanical design of the reactor in the form of a general arrangement drawing with supplementary detail drawings to show essential constructional features. Include recommendations for the feed of gaseous ammonia, carbon dioxide and carbamate solution, the latter being very corrosive. The design should ensure good gas-liquid contact; suitable instrumentation should be suggested, and provision included for its installation. Access must be possible for maintenance.
8. Specify suitable control systems for the maintenance of constant conditions in the reactor against a 15 per cent change in input rate of ammonia or carbon dioxide, and examine the effect of such a change, if uncorrected, on the steam generation capability of the high-pressure condenser.

## REFERENCES

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2. PAYNE, A. J. and CANNER, J. A. *Chemical and Process Engineering*, May 1969, pp. 81-88.
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## F.6 HYDROGEN FROM FUEL OIL

### The project

A plant is to be designed to produce 20 million standard cubic feet per day ( $0.555 \times 10^6$  standard  $\text{m}^3/\text{day}$ ) of hydrogen of at least 95 per cent purity. The process to be employed is the partial oxidation of oil feedstock.<sup>1–3</sup>

### Materials available

(1) Heavy fuel oil feedstock of viscosity 900 seconds Redwood One ( $2.57 \times 10^{-4} \text{ m}^2/\text{s}$ ) at  $100^\circ\text{F}$  with the following analysis:

Carbon	85 per cent wt
Hydrogen	11 per cent wt
Sulphur	4 per cent wt
Calorific value	18,410 Btu/lb (42.9 MJ/kg)
Specific gravity	0.9435

The oil available is pumped from tankage at a pressure of 30 psig ( $206.9 \text{ kN/m}^2$  gauge) and at  $50^\circ\text{C}$ .

(2) Oxygen at 95 per cent purity (the other component assumed to be wholly nitrogen) and at  $20^\circ\text{C}$  and 600 psig ( $4140 \text{ kN/m}^2$  gauge).

### Services available

- (1) Steam at 600 psig ( $4140 \text{ kN/m}^2$  gauge) saturated.
- (2) Cooling water at a maximum summer temperature of  $25^\circ\text{C}$ .
- (3) Demineralised boiler feedwater at 20 psig ( $138 \text{ kN/m}^2$  gauge) and  $15^\circ\text{C}$  suitable for direct feed to the boilers.
- (4) Electricity at 440 V, three-phase 50 Hz, with adequate incoming cable capacity for all proposed uses.
- (5) Waste low-pressure steam from an adjacent process.

### On-stream time

8050 hours/year.

### Product specification

Gaseous hydrogen with the following limits of impurities:

CO	1.0 per cent vol maximum (dry basis)
CO <sub>2</sub>	1.0 per cent vol maximum (dry basis)
N <sub>2</sub>	2.0 per cent vol maximum (dry basis)
CH <sub>4</sub>	1.0 per cent vol maximum (dry basis)
H <sub>2</sub> S	Less than 1 ppm

The gas is to be delivered at 35°C maximum temperature, and at a pressure not less than 300 psig (2060 kN/m<sup>2</sup> gauge). The gas can be delivered saturated, i.e. no drying plant is required.

### ***The process***

Heavy fuel oil feedstock is delivered into the suction of metering-type ram pumps which feed it via a steam preheater into the combustor of a refractory-lined flame reactor. The feedstock must be heated to 200°C in the preheater to ensure efficient atomisation in the combustor. A mixture of oxygen and steam is also fed to the combustor, the oxygen being preheated in a separate steam preheater to 210°C before being mixed with the reactant steam.

The crude gas, which will contain some carbon particles, leaves the reactor at approximately 1300°C and passes immediately into a special waste-heat boiler where steam at 600 psig (4140 kN/m<sup>2</sup> gauge) is generated. The crude gas leaves the waste heat boiler at 250°C and is further cooled to 50°C by direct quenching with water, which also serves to remove the carbon as a suspension. The analysis of the quenched crude gas is as follows:

H <sub>2</sub>	47.6	per cent vol (dry basis)
CO	42.1	per cent vol (dry basis)
CO <sub>2</sub>	8.3	per cent vol (dry basis)
CH <sub>4</sub>	0.1	per cent vol (dry basis)
H <sub>2</sub> S	0.5	per cent vol (dry basis)
N <sub>2</sub>	1.40	per cent vol (dry basis)
	<u>100.0</u>	per cent vol (dry basis)

For the primary flame reaction steam and oxygen are fed to the reactor at the following rates:

Steam	0.75	kg/kg of heavy fuel oil feedstock
Oxygen	1.16	kg/kg of heavy fuel oil feedstock

The carbon produced in the flame reaction, and which is subsequently removed as carbon suspension in water, amounts to 1.5 per cent by weight of the fuel oil feedstock charge. Some H<sub>2</sub>S present in the crude gas is removed by contact with the quench water.

The quenched gas passes to an H<sub>2</sub>S removal stage where it may be assumed that H<sub>2</sub>S is selectively scrubbed down to 15 parts per million with substantially nil removal of CO<sub>2</sub>. Solution regeneration in this process is undertaken using the waste low-pressure steam from another process. The scrubbed gas, at 35°C and saturated, has then to undergo CO conversion, final H<sub>2</sub>S removal, and CO<sub>2</sub> removal to allow it to meet the product specification.

CO conversion is carried out over chromium-promoted iron oxide catalyst employing two stages of catalytic conversion; the plant also incorporates a saturator and desaturator operating with a hot water circuit.

Incoming gas is introduced into the saturator (a packed column) where it is contacted with hot water pumped from the base of the desaturator; this process serves to preheat the gas and to introduce into it some of the water vapour required as reactant. The gas then passes to two heat exchangers in series. In the first, the unconverted gas is heated

against the converted gas from the second stage of catalytic conversion; in the second heat exchanger the unconverted gas is further heated against the converted gas from the first stage of catalytic conversion. The remaining water required as reactant is then introduced into the unconverted gas as steam at 600 psig (4140 kN/m<sup>2</sup> gauge) saturated and the gas/steam mixture passes to the catalyst vessel at a temperature of 370°C. The catalyst vessel is a single shell with a dividing plate separating the two catalyst beds which constitute the two stages of conversion. The converted gas from each stage passes to the heat exchangers previously described and thence to the desaturator, which is a further packed column. In this column the converted gas is contacted countercurrent with hot water pumped from the saturator base; the temperature of the gas is reduced and the deposited water is absorbed in the hot-water circuit. An air-cooled heat exchanger then reduces the temperature of the converted gas to 40°C for final H<sub>2</sub>S removal.

Final H<sub>2</sub>S removal takes place in four vertical vessels each approximately 60 feet (18.3 m) in height and 8 feet (2.4 m) in diameter and equipped with five trays of iron-oxide absorbent. Each vessel is provided with a locking lid of the autoclave type. The total pressure drop across these vessels is 5 psi (35 kN/m<sup>2</sup>). Gas leaving this section of the plant contains less than 1 ppm of H<sub>2</sub>S and passes to the CO<sub>2</sub> removal stage at a temperature of 35°C.

CO<sub>2</sub> removal is accomplished employing high-pressure potassium carbonate wash with solution regeneration.<sup>4</sup>

## Data

### ***I. Basic data for CO conversion section of the plant***

#### *(a) Space velocity*

The space velocity through each catalyst stage should be assumed to be 3500 volumes of gas plus steam measured at NTP per volume of catalyst per hour. It should further be assumed that use of this space velocity will allow a 10°C approach to equilibrium to be attained throughout the possible range of catalyst operating temperatures listed below.

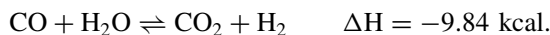
#### *(b) Equilibrium data for the CO conversion reaction*

For

$$K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} \times p_{\text{H}_2}}$$

Temp. (K)	$K_p$
600	$3.69 \times 10^{-2}$
700	$1.11 \times 10^{-1}$
800	$2.48 \times 10^{-1}$

#### *(c) Heat of reaction*



### ***II. Basic data for CO<sub>2</sub> removal using hot potassium carbonate solutions***

The data presented in Ref. 4 should be employed in the design of the CO<sub>2</sub> removal section of the plant. A solution concentration of 40 per cent wt equivalent K<sub>2</sub> CO<sub>3</sub> should be employed.

## Scope of design work required

### 1. Process design

- (a) Calculate, and prepare a diagram to show, the gas flows, compositions, pressures and temperatures, at each main stage throughout the processes of gasification and purification.
- (b) Prepare a mass balance diagram for the CO conversion section of the plant including the live steam addition to the unconverted gas. Basic data which should be employed for the CO conversion process are presented in the Appendix.
- (c) Prepare an energy-balance diagram for the flame reactor and for the associated waste-heat boiler.
- (d) Prepare a process flow-diagram showing all major items of equipment. This need not be to scale but an indication of the internal construction of each item (with the exception of the flame reactor, waste-heat boiler and quench tower) should be given. The primary H<sub>2</sub>S removal stage need not be detailed.
- (e) Prepare an equipment schedule for the CO conversion section of the plant, specifying major items of equipment.

### 2. Chemical engineering design

- (a) Prepare a detailed chemical engineering design of the absorber on the CO<sub>2</sub> removal stage.
- (b) Prepare a chemical engineering design for the saturator on the CO conversion section.

### 3. Mechanical design

Make recommendations for the mechanical design of the CO<sub>2</sub> removal absorber, estimating the shell and end-plate thickness and showing, by means of sketches suitable for submission to a design office, how:

- (a) the beds of tower packing are supported,
- (b) the liquid is distributed.

Develop a detailed mechanical design of the CO conversion reactor, paying particular attention to the choice of alloy steels versus refractory linings, provisions for thermal expansion, inlet gas distribution, catalyst bed-support design, facilities for charging and discharging catalyst and provisions for instrumentation.

### 4. Control

Prepare a full instrumentation of flow-sheet of the CO conversion section of the plant, paying particular attention to the methods of controlling liquid levels in the circulating water system and temperatures in the catalyst beds. Derive the unsteady-state equations which would have to be employed in the application of computer control to the CO conversion section of the plant.

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3. S. C. SINGER and L. W. TER HAAR, *Chem. Eng Prog.*, 1961, **57**, pp. 68–74. Reducing gases by partial oxidation of hydrocarbons.
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## F.7 CHLORINE RECOVERY FROM HYDROGEN CHLORIDE

### The project

A plant is to be designed for the production of 10,000 tonnes per annum of chlorine by the catalytic oxidation of HCl gas.

### Materials available

- (1) HCl gas as by-product from an organic synthesis process. This may be taken to be 100 per cent pure and at 20°C and absolute pressure of 14.7 psi (100 kN/m<sup>2</sup>).
- (2) Air. This may be taken to be dry and at 20°C and absolute pressure of 14.7 psi (100 kN/m<sup>2</sup>).

### Services available

- (1) Steam at 200 psig (1400 kN/m<sup>2</sup>).
- (2) Cooling water at a maximum summer temperature of 24°C.
- (3) A limited supply of cooling water at a constant temperature of 13°C is also available.
- (4) Electricity at 440 V, three-phase, 50 Hz.

### On-stream time

8000 hours/year.

### Product specification

Gaseous chlorine mixed with permanent gases and HCl. The HCl content not to exceed  $5 \times 10^{-5}$  part by weight of HCl per unit weight of chlorine.

### The process

HCl is mixed with air and fed into a fluidness bed reactor containing cupric chloride/pumice catalyst and maintained at a suitable temperature in the range 300–400°C. The HCl in the feed is oxidised, and the chlorine and water produced in the reaction, together with unchanged HCl and permanent gases, are passed to a packed tower cooler/scrubber, operating somewhat above atmospheric pressure, where they are contacted with aqueous HCl containing 33–36 per cent by weight of HCl. This acid enters the cooler/scrubber at about 20°C. Most of the water and some of the HCl contained in the gases entering the cooler/scrubber are dissolved in the acid. The liquid effluent from the base of the cooler/scrubber flows to a divider box from which one stream passes to the top of the cooler/scrubber, via a cooler which lowers its temperature to 20°C, and another

stream passes to a stripping column (“expeller”). Gas containing 98 per cent by weight of HCl (the other constituents being water and chlorine) leaves the top of the expeller and is recycled to the reactor. A mixture of water and HCl containing 20–22 per cent by weight of HCl leaves the base of the expeller. This liquid passes, *via* a cooler, to the top of an HCl absorber, which is required to remove almost the whole of the HCl contained in the gases leaving the cooler/scrubber. The liquid leaving the base of the HCl absorber, containing 33–36 per cent by weight of HCl, is divided into two streams, one of which flows to the expeller while the other is collected as product. The gaseous chlorine leaving the top of the HCl absorber passes to a drier.

## Data

### Reactor

Catalyst particle size distribution (U.S. Patent 2746 844/1956)

Size range ( $\mu\text{m}$ )	Cumulative weight percentage undersize (at upper limit)
50–100	0.39
100–150	15.0
150–200	58.0
200–250	85.0
250–300	96.6
300–350	99.86

Density of catalyst: 40 lb/ft<sup>3</sup> (640 kg/m<sup>3</sup>).

Voidage at onset of fluidisation: 0.55.

Particle shape factor: 0.7.

Heat of reaction: 192 kcal/kg of HCl ( $\Delta H = -29,340$  kJ/kmol).

(Arnold, C. W. and Kobe, K. A., *Chem. Eng. Prog.*, 1952, **48**, 293.)

Gas residence time in reactor: 25 seconds,

Quant, J. *et al.*, *Chem. Engr, Lond.*, 1963, p. CE224.

### Cooler/scrubber and expeller

The overall heat-transfer coefficient between the gas and liquid phases can be taken to be 5.0 Btu/h ft<sup>2</sup> degF (28 W/m<sup>2</sup> °C).

### Scope of design work required

1. Prepare a mass balance diagram for the process, up to but not including the drier, on the basis of weight/hour. Base the calculation on 10,000 long tons/year of chlorine entering the drier together with permanent gases, water and not more than  $5 \times 10^{-5}$  parts by weight of HCl per unit weight of chlorine.
2. Prepare an energy balance diagram for the reactor and cooler/scrubber system.
3. Prepare a process flow diagram, up to but not including the drier, showing all the major items of equipment, with indications of the type of internal construction, as



- far as possible in the corrected evaluation. The diagram should show all major pipe lines and the instrumentation of the reactor and the cooler/scrubber system.
4. Prepare an equipment schedule listing all major items of equipment and giving sizes, capacities, operating pressures and temperatures, materials of construction, etc.
  5. Present a specimen pipeline sizing calculation.
  6. Work out the full chemical engineering design of the reactor and cooler/scrubber systems.
  7. Calculate the height and diameter of the expeller.
  8. Prepare a mechanical design of the cooler/scrubber showing by dimensioned sketches suitable for submission to a draughtsman how:
    - (a) The tower packing is to be supported.
    - (b) The liquid is to be distributed in the tower.
    - (c) The shell is to be constructed so as to withstand the severely corrosive conditions inside it.
  9. Discuss the safety precautions involved in the operation of the plant, and the procedure to be followed in starting the plant up and shutting it down.
  10. Develop the mechanical design of the reactor and prepare a key arrangement drawing, supplemented by details to make clear the essential constructional features. The study should include recommendations for the design of the bed and means of separation and disposal of dust from the exit gas stream, and should take account of needs connected with thermal expansion, inspection, maintenance, starting and stopping, inlet gas distribution, insertion and removal of catalyst, and the positioning and provision for reception of instruments required for control and operational safety. Written work should be confined, as far as possible, to notes on engineering drawings, except for the design calculations, the general specification and the justification of materials of construction.
  11. Assuming that the plant throughout may vary by 10 per cent on either side of its normal design value due to changes in demand, specify control systems for:
    - (i) regulation of the necessary recycle flow from the cooler/scrubber base, at the design temperature; and
    - (ii) transfer of the cooler/scrubber make liquor to the expeller.

## REFERENCES

- ARNOLD, C. W. and KOBE, K. A. (1952) *Chem. Engng Prog.* **48**, 293.  
FLEURKE, K. H. (1968) *Chem. Engr., Lond.*, p. CE41.  
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SCONCE, J. S. (1962) *Chlorine: Its Manufacture, Properties, and Uses* (New York: Rheinhold Publishing Corporation).

## F.8 ANILINE FROM NITROBENZENE

### The project

Design a plant to make 20,000 tonnes per annum of refined aniline by the hydrogenation of nitro-benzene. The total of on-stream operation time plus regeneration periods will be 7500 hours per year.

**Materials available:**

Nitrobenzene containing < 10 ppm thiophene.

Hydrogen of 99.5 per cent purity at a pressure of 50 psig (350 kN/m<sup>2</sup>).

Copper on silica gel catalyst.

**Services available:**

Steam at 200 psig (1400 kN/m<sup>2</sup>) 197°C, and 40 psig (280 kN/m<sup>2</sup>) 165°C.

Cooling water at a maximum summer temperature of 24°C.

Town's water at 15°C.

Electricity at 440 V, three-phase 50 Hz.

**Product specification:**

Aniline	99.9 per cent w/w min.
Nitrobenzene	2 ppm max.
Cyclohexylamine	100 ppm max.
Water	0.05 per cent w/w max.

**The process**

Nitrobenzene is fed to a vaporiser, where it is vaporised in a stream of hydrogen (three times stoichiometric). The mixture is passed into a fluidness bed reactor containing copper on silica gel catalyst, operated at a pressure, above the bed, of 20 psig (140 kN/m<sup>2</sup>). The contact time, based on superficial velocity at reaction temperature and pressure and based on an unexpanded bed, is 10 seconds. Excess heat of reaction is removed to maintain the temperature at 270°C by a heat-transfer fluid passing through tubes in the catalyst bed. The exit gases pass through porous stainless-steel candle filters before leaving the reactor.

The reactor gases pass through a condenser/cooler, and the aniline and water are condensed. The excess hydrogen is recycled, except for a purge to maintain the impurity level in the hydrogen to not more than 5 per cent at the reactor inlet. The crude aniline and water are let down to atmospheric pressure and separated in a liquid/liquid separator, and the crude aniline containing 0.4 per cent unreacted nitrobenzene and 0.1 per cent cyclo-hexylamine as well as water, is distilled to give refined aniline. Two stills are used, the first removing water and lower boiling material, and the second removing the higher boiling material (nitrobenzene) as a mixture with aniline. The vapour from the first column is condensed, and the liquid phases separated to give an aqueous phase and an organic phase. A purge is taken from the organic stream to remove the cyclo-hexylamine from the system, and the remainder of the organic stream recycled. The cyclo-hexylamine content of the purge is held to not greater than 3 per cent to avoid difficulty in phase separation. In the second column, 8 per cent of the feed is withdrawn as bottoms product.

The purge and the higher boiling mixture are processed away from the plant, and the recovered aniline returned to the crude aniline storage tank. The aniline recovery efficiency in the purge unit is 87.5 per cent, and a continuous stream of high-purity aniline may be assumed.

The aqueous streams from the separators (amine-water) are combined and steam stripped to recover the aniline, the stripped water, containing not more than 30 ppm aniline or 20 ppm cyclo-hexylamine, being discharged to drain.

Regeneration of the catalyst is accomplished in place using air at 250–350°C to burn off organic deposits. Regeneration takes 24 hours, including purging periods.

The overall yield of aniline is 98 per cent theory from nitrobenzene, i.e. from 100 mols of nitrobenzene delivered to the plant, 98 mols of aniline passes to final product storage.

### Scope of design work required

1. Prepare a material balance on an hourly basis for the complete process in weight units.
2. Prepare a heat balance for the reactor system, comprising vaporiser, reactor and condenser/cooler.
3. Draw a process flow diagram for the plant. This should show all items of equipment approximately to scale and at the correct elevation. The catalyst regeneration equipment should be shown.
4. Chemical engineering design.

*(a) Vaporiser*

Give the detailed chemical engineering design, and give reasons for using the type chosen. Specify the method of control.

*(b) Reactor*

Give the detailed chemical engineering design for the fluidness bed and heat transfer surfaces. Select a suitable heat transfer fluid and give reasons for your selection. Do *not* attempt to specify the filters or to design the condenser/cooler in detail.

*(c) Crude aniline separator*

Specify the diameter, height and weir dimensions and sketch the method of interface level control which is proposed.

*(d) Amine water stripper*

Give the detailed chemical engineering design of the column.

5. Prepare a full mechanical design for the reactor. Make a dimensioned sketch suitable for submission to a drawing office, which should include details of the distributor, and show how the heat transfer surfaces will be arranged. An indication of the method of supporting the candle filters should be shown, but do not design this in detail.
6. Prepare an equipment schedule detailing all major items of equipment, including tanks and pumps. A specimen pipeline sizing calculation for the reactor inlet pipe should be given. All materials of construction should be specified.
7. Describe briefly how the plant would be started up and shut down, and discuss safety aspects of operation.
8. Write a short discussion, dealing particularly with the less firmly based aspects of the design, and indicating the semi-technical work which is desirable.

**Data**

## 1. Catalyst properties:

## (a) Grading:

0–20 $\mu\text{m}$ :	Negligible
20–40 $\mu\text{m}$ :	3 per cent w/w
40–60 $\mu\text{m}$ :	7 per cent w/w
60–80 $\mu\text{m}$ :	12 per cent w/w
80–100 $\mu\text{m}$ :	19 per cent w/w
100–120 $\mu\text{m}$ :	25 per cent w/w
120–140 $\mu\text{m}$ :	24 per cent w/w
140–150 $\mu\text{m}$ :	10 per cent w/w
> 150 $\mu\text{m}$ :	Negligible.

(b) Voidage at minimum fluidisation, 0.45.

(c) Shape factor, 0.95.

(d) Bulk density at minimum fluidisation, 50 lb/ft<sup>3</sup> (800 kg/m<sup>3</sup>).

(e) Life between regenerations 1500 tonne of aniline per ton of catalyst, using the feedstock given.

2. Exothermic heat of hydrogenation.  $-\Delta H_{298} = 132,000$  CHU/lb mol (552,000 kJ/k mol).

3. Mean properties of reactor gases at reactor conditions:

Viscosity	0.02 centipoise (0.02 mNs/m <sup>2</sup> )
Heat capacity at constant pressure	0.66 CHU/lb <sup>o</sup> C (2.76 kJ/kg <sup>o</sup> C)
Thermal conductivity	0.086 CHU/hr ft <sup>2</sup> ( <sup>o</sup> C/ft) (0.15 W/m <sup>o</sup> C)

4. Pressure drop through candle filters = 5 psi (35 kN/m<sup>2</sup>).

5. Density of nitrobenzene:

Temp. <sup>o</sup> C	Density g/cm <sup>3</sup>
0	1.2230
15	1.2083
30	1.1934
50	1.1740

6. Latent heat of vaporisation of nitrobenzene:

Temp. <sup>o</sup> C	Latent heat CHU/lb	(kJ/kg)
100	104	(434)
125	101	(422)
150	97	(405)
175	92.5	(387)
200	85	(355)
210	79	(330)

7. Latent heat of vaporisation of aniline:

Temp. °C	Latent heat CHU/lb	(kJ/kg)
100	133.5	(558)
125	127	(531)
150	120	(502)
175	110	(460)
183	103.7	(433)

8. Specific heat of aniline vapour = 0.43 CHU/lb°C (1.80 kJ/kg°C).

9. Solubility of aniline in water:

Temp. °C	per cent w/w aniline
20	3.1
40	3.3
60	3.8
100	7.2

10. Solubility of water in aniline:

Temp. °C	per cent w/w water
20	5.0
40	5.3
60	5.8
100	8.4

11. Density of aniline/water system:

Temp. °C	Density g/cm <sup>3</sup>	
	Water layer	Aniline layer
0	1.003	1.035
10	1.001	1.031
20	0.999	1.023
30	0.997	1.014
40	0.995	1.006
50	0.991	0.998
60	0.987	0.989
70	0.982	0.982

12. Partition of cyclo-hexylamine between aniline and water at 30°C:

w/w per cent cyclo-hexylamine in aniline	w/w per cent water in aniline	w/w per cent cyclo-hexylamine in water	w/w per cent aniline in water
1.0	5.7	0.12	3.2
3.0	6.6	0.36	3.2
5.0	7.7	0.57	3.2

13. Partition coefficient of nitrobenzene between aniline layer and water layer:

$$C_{a.l.}/C_{w.l.} = 300.$$

14. Design relative velocity in crude aniline-water separator: 10 ft/h (3 m/h).  
 15. Equilibrium data for water-aniline system at 760 mm Hg abs:

Temp °C	Mole fraction water	
	Liquid	Vapour
184	0	0
170	0.01	0.31
160	0.02	0.485
150	0.03	0.63
140	0.045	0.74
130	0.07	0.82
120	0.10	0.88
110	0.155	0.92
105	0.20	0.94
100	0.30	0.96
99	0.35–0.95	0.964
	0.985	0.9641
	0.9896	0.9642
	0.9941	0.9735
	0.9975	0.9878
	0.9988	0.9932

16. Equilibrium data for cyclo-hexylamine-water system at 760 mm Hg abs:

Mole fraction cyclo-hexylamine	
Liquid	Vapour
0.005	0.065
0.010	0.113
0.020	0.121
0.030	0.123
0.040	0.124
0.050	0.125
0.100	0.128
0.150	0.131
0.200	0.134
0.250	0.137

17. Temperature coefficient for aniline density— $0.054 \text{ lb/ft}^3 \text{ } ^\circ\text{C}$  ( $0.86 \text{ kg/m}^3 \text{ } ^\circ\text{C}$ ) (range  $0\text{--}100^\circ\text{C}$ ).

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- LEVA, M. *Fluidization*, 1959 (New York: McGraw-Hill Book Company, Inc.).
- ROTTENBURG, P. A. *Trans. Instn. Chem Engrs*, 1957, **35**, 21.  
 As an alternative to Reference 1 above, any of the following may be read as background information to the process:
- Hyd. Proc. and Pet. Ref.*, 1961, **40**, No. 11, p. 225.
- STEPHENSON, R. M. *Introduction to the Chemical Process Industries*, 1966 (New York: Reinhold Publishing Corporation).
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## APPENDIX G

# *Equipment Specification (Data) Sheets*

- (1) Vessel data sheet
- (2) Column tray data sheet
- (3) Heat exchanger data sheet
- (4) Plate heat exchanger data sheet
- (5) Centrifugal pump data sheet
- (6) Reciprocating pump data sheet
- (7) Rotary positive pump data sheet
- (8) Mixer data sheet
- (9) Conveyor data sheet
- (10) Relief and safety valve data sheet

### Design Data Sheets

- (1) Data sheet for pressure vessel design

Vessel data sheet										Equipment No. (Tag)		
(PROCEED)										Descript. (Func.)		
										Sheet No.		
Operating Data												1
												2
No. REQUIRED				CAPACITY								3
SPECIFIC GRAVITY OF CONTENTS				COMPUTED (yes or no)								4
			SHELL			JACKET FULL/HALF COIL			INTERNAL COIL			5
CONTENTS												6
DIAMETER												7
LENGTH												8
DESIGN CODE												9
MAX. WORKING PRESSURE												10
DESIGN PRESSURE												11
MAX. WORKING TEMP												12
DESIGN TEMP												13
TEST PRESSURE (HYDROSTATIC)												14
TEST PRESSURE (AIR)												15
MATERIALS												16
JOINT FACTOR												17
CORROSION ALLOWANCE												18
THICKNESS												19
END TYPE			THICKNESS			JOINT FACTOR						20
END TYPE			THICKNESS			JOINT FACTOR						21
TYPE OF SUPPORT			THICKNESS			MATERIAL						22
WIND LOAD DESIGN			RADIOGRAPHY %			STRESS RELIEF						23
INTERNAL BOLTS MATERIAL			TYPE			NUTS						24
EXTERNAL BOLTS MATERIAL			TYPE			NUTS						25
INSULATION (SEP. ORDER)			INSULATION FITTING ATTACHMENT BY									26
GASKET MATERIAL			INSPECTION BY									27
PAINTING												28
WEIGHT			EMPTY									29
FULL OF LIQUID			OPERATING									30
INTERNALS and EXTERNALS			DATE OF ENQUIRY			DATE OF ORDER						31
ORDER No.			DRG. No.									32
MANUFACTURER												33
REMARKS AND NOTES:- UNLESS OTHERWISE STATED ALL FLANGE BOLT HOLES TO BE												34
OFF-CENTRE OF VESSEL CENTRE LINES N/S and E/W (NOT RADIALY)												35
												37
												38
												39
												40
A												41
B												42
C												43
D												44
E												45
F												46
G												47
H												48
H												49
K												50
K												51
M												52
N												53
P												54
REF	No.	DUTY		NOM BORE	PIPE WALL	TYPE	CLASS	MATERIAL	BRANCH	REMARKS		55
BRANCH		DUTY		mm/Ins	THICKNESS	RANGE SPEC			COMPEN'N	REMARKS		56
												57
Prepared				3			6					58
Checked				2			5					59
Approved				1			4					60
	Date	Engineering	Process	REV	By	Appr.	Date	REV	By	Appr.	Date	61
Service				Company				Address				62
Equipment No.												63
Project No.												64



Column Tray data sheet								Equipment No. (Tag)			
(PROCEED)								Descript. (Func.)			
Operating Data								Sheet No.			
TOP				BOTTOM				OR TOP AND BOTTOM		1	
TOWER INSIDE DIAMETER (Inches) (mm)										2	
TRAY SPACE (Inches) (mm)										3	
TOTAL TRAYS IN SECTION										4	
Internal Conditions at Tray Number										5	
VAPOUR TO TRAY										6	
RATE (lb/hr) (kg/hr)										7	
DENSITY (lb/ft <sup>3</sup> ) (kg/m <sup>3</sup> )										8	
PRESSURE (psi) (kg/cm <sup>2</sup> ) (Bar g) (Bar a)										9	
TEMPERATURE (°F) (°C)										10	
LIQUID FROM TRAY										11	
RATE (lb/hr) (kg/m <sup>3</sup> )										12	
DENSITY (lb/ft <sup>3</sup> ) (kg/m <sup>3</sup> )										13	
TEMPERATURE (°F) (°C)										14	
VISCOSITY cP										15	
NUMBER OF LIQUID FLOW PATHS										16	
Technical/Mechanical Data										17	
TOWER MANHOLE INSIDE DIAMETER (Inches) (mm)										18	
TRAY MATERIAL										19	
TRAY THICKNESS										20	
CAP MATERIAL										21	
HOLDDOWN MATERIAL										22	
NUTS and BOLTS MATERIAL										23	
SUPPORT RING MATERIAL										24	
SUPPORT RING SIZE (Inches) (mm)										25	
DOWNCOMER BOLT BAR THICKNESS (Inches) (mm)										26	
CORROSION ALLOWANCE										27	
TRAYS (Inches) (mm)										28	
TOWER ATTACHMENTS (Inches) (mm)										29	
TRAYS NUMBERED FROM TOP TO BOTTOM										30	
TRAY MANWAY REMOVAL FROM										31	
DATE OF ENQUIRY				DATE OF ORDER						32	
ORDER No.				DRG. No.						33	
MANUFACTURER										34	
NOTES										35	
(1) INTERNAL VAPOUR AND LIQUID LOADINGS AT THE LIMITING SECTIONS ARE REQUIRED TO ENSURE PROPER TRAY DESIGN.										36	
DENSITIES ARE REQUIRED AT ACTUAL INSIDE TOWER CONDITIONS OF TEMPERATURE and PRESSURE. VISCOSITY IS NOT										37	
REQUIRED UNLESS GREATER THAN 0.7 cp										38	
(2) CROSS OUT DIMENSION UNITS WHICH DO NOT APPLY. TRAY SUPPLIER TO ADVISE.										39	
REMARKS										40	
Prepared										41	
Checked										42	
Approved										43	
Date				Engineering				Process			
REV				By				Appr.			
Date				REV				By			
Date				Appr.				Date			
Service				Company				Address			
Equipment No.											
Project No.											

Heat Exchanger data sheet										(PROCEED)		Equipment No. (Tag)	
												Descript. (Func.)	
												Sheet No.	
Operating Data												1	
												2	
SIZE		TYPE		No. OF UNITS								3	
SHELLS PER UNIT		HORIZONTAL CONNECTED IN (parallel or series)										4	
SURFACE PER UNIT		SURFACE PER SHELL										5	
												6	
Performance of one Unit												7	
				SHELL SIDE				TUBE SIDE				8	
FLUID CIRCULATING												9	
TOTAL FLUID ENTERING												10	
		IN		OUT		IN		OUT				11	
VAPOUR												12	
LIQUID												13	
STEAM												14	
WATER												15	
NON-CONDENSABLES												16	
FLUID VAPOURISED OR CONDENSED												17	
SPECIFIC GRAVITY LIQUID												18	
Mol Wt VAPOUR												19	
Mol Wt NON-CONDENSABLES												20	
VISCOSITY LIQUID												21	
LATENT HEAT												22	
SPECIFIC HEAT												23	
THERMAL CONDUCTIVITY												24	
TEMPERATURE												25	
OPERATING PRESSURE												26	
VELOCITY												27	
No. OF PASSES												28	
PRESSURE DROP		ALLOW		CALC.		ALLOW		CALC.				29	
FOULING RESISTANCE												30	
HEAT EXCHANGED						MTD (CORRECTED)						31	
TRANSFER RATE SERVICE						CLEAN						32	
												33	
Construction of one Shell												34	
DESIGN PRESSURE												35	
TEST PRESSURE												36	
DESIGN TEMPERATURE												37	
METAL TEMPERATURE												38	
TUBES		No. OD		THICKNESS		LENGTH		PITCH				39	
SHELL		LD.						SHELL COVER				40	
CHANNEL		CHANNEL COVER						FLTNG HEAD COVER				41	
TUBE SHEET STATIONARY								FLOATING				42	
BAFFLES CROSS		TYPE						SPACING % CUT				43	
TUBE SUPPORTS		TYPE						SPACING				44	
LONG BAFFLE		TYPE						SEAL				45	
IMPINGEMENT BAFFLE		TYPE						SEAL STRIPS				46	
TYPE OF JOINT		TUBE						TUBE ATTACHMT				47	
GASKETS SHELL IN		CHANNEL						FLOATING HEAD				48	
CONNECTIONS SHELL IN		INTERCONN						SHELL OUT				49	
CONNECTIONS CHANNEL IN		INTERCONN						CHANNEL OUT				50	
CORROSION ALLOWABLE SHELL SIDE								TUBE SIDE				51	
EXPANSION BELLOWES		BOLTS						NUTS				52	
DESIGN CODE		X-RAY						S.R.				53	
INSPECTION		PAINTING						INSULATION				54	
WEIGHT OF ONE UNIT EMPTY		OPERATING						DATE OF ENQUIRY				55	
DATE OF ORDER		ORDER No.						DRG. No.				56	
INSPECTION FITTING ATTACHMENT BY								MANUFACTURER				57	
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Centrifugal Pump data sheet										Equipment No. (Tag)	
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										Sheet No.	
<b>Operating Data</b>											1
NUMBER OF MACHINES											2
TYPE											3
LIQUID											4
AVAILABLE N.P.S.H.											5
CAPACITY											6
PRESSURES											7
ELECTRICAL SUPPLY											8
COOLING WATER SUPPLY											9
SEALING WATER SUPPLY											10
STEAM SUPPLY											11
VISCOSITY											12
Sp GRAVITY											13
VAPOUR PRESSURE											14
WORKING TEMPERATURE											15
pH											16
ANALYSIS											17
											18
<b>Technical Data</b>											19
PUMP DRAWING No.											20
SPEED rpm											21
SAFE MINIMUM FLOW											22
SHUT OFF HEAD											23
N.P.S.H.											24
PUMP EFFICIENCY											25
PERFORMANCE CURVE No.											26
DRTN OF ROTN (FACING COUPLING)											27
TYPE OF GLAND OR SEAL											28
BALANCE ARRANGEMENT											29
COOLING WATER REQUIRED											30
SEALING WATER REQUIRED											31
DETAILS OF CONNECTIONS											32
SUCTION											33
DISCHARGE											34
TYPE OF COUPLING GUARD											35
TYPE OF THRUST BEARING											36
TYPE OF JOURNAL BEARING											37
TYPE OF GEAR AND MAKER											38
FULL LOAD TORQUE											39
STARTING TORQUE											40
IMPELLER SIZE (MIN.)											41
											42
<b>Materials of Construction</b>											43
SHAFT											44
IMPELLER											45
BALANCE DISC OR PISTON											46
IMPELLER WEAR RINGS											47
CASING WEARING RINGS											48
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<b>Design Standards and Inspection</b>											51
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Reciprocating Pump data sheet										Equipment No. (Tag)		
										(PROCEED)		
										Descript. (Func.)		
										Sheet No.		
<b>Operating Data</b>											1	
											2	
NUMBER OF MACHINES		Installed		working						standby	3	
TYPE											4	
LIQUID											5	
AVAILABLE N.P.S.H.	Bar a										6	
CAPACITY		max.		min.						normal	7	
PRESSURES		suction		discharge						different	8	
ELECTRICAL SUPPLY		Volts		phase						cycles	9	
COOLING WATER SUPPLY		press.		temp.						flow	10	
SEALING WATER SUPPLY		press.		temp.						flow	11	
STEAM SUPPLY		press.		temp.						flow	12	
VISCOSITY		⊙		press.						temp.	13	
Sp GRAVITY		⊙		press.						temp.	14	
VAPOUR PRESSURE									⊙	temp.	15	
WORKING TEMPERATURE	pH										16	
ANALYSIS											17	
<b>Technical Data</b>											18	
											19	
PUMP DRAWING No.				MAX. ABSORBED POWER REQD.							20	
SPEED rpm				EFFICIENCY							21	
PLUNGER DIA and SPEED				MAX. RECOMMENDED kW OF DRIVER							22	
STROKE				INSTALLED kW OF DRIVER							23	
N.P.S.H. REQUIRED				SPEED OF DRIVER							24	
CAPACITY CONTROL				SPEED RATIO							25	
TYPE OF DRIVE				DIR'N OF ROTN (FACING COUPLING)							26	
TYPE OF GLAND				DETAILS OF LUBRICATOR							27	
TYPE VALVES				TYPE OF BASEPLATES							28	
COOLING WATER REQUIRED				RELIEF VALVE SET PRESSURE							29	
SEALING WATER REQUIRED				TYPE OF BEARINGS							30	
DETAILS OF CONNECTIONS				SUPPLIER OF DRIVER							31	
SUCTION				COUPLING							32	
DISCHARGE				DRIVER HALF COUPLING FITTED BY							33	
STARTING TORQUE				TYPE OF COUPLING and MAKER							34	
TYPE OF GEAR and MAKER				TYPE OF TORQUE CONVERTER and MAKER							35	
TYPE OF DRIVE				DIRECT				GEAR			36	
<b>Materials of Construction</b>											37	
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CYLINDERS				CRANK CASE							39	
VALVE HEAD				CRANKSHAFT							40	
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GLAND CASING				BASEPLATE							46	
GLAND PACKING				RELIEF VALVE							47	
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<b>Design Standards and Inspection</b>											49	
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DESIGN CODE				MAX. ERECTION WEIGHT							51	
HYDROSTATIC TEST PRESS.				SHIPPING WEIGHT							52	
INSPECTION REQUIREMENTS				SHIPPING VOLUME							53	
DRG. and DATA REQUIREMENTS				TOTAL WEIGHT							54	
DATE OF ENQUIRY				DATE OF ORDER							55	
DRG. No.				ORDER No.							56	
MANUFACTURER											57	
Prepared				3				6			58	
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Service				Company				Address				62
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Mixer data sheet										Equipment No. (Tag)		
(PROCEED)										Descript. (Func.)		
										Sheet No.		
<b>Operating Data</b>											1	
											2	
No. OF MACHINES		WORKING			STANDBY						3	
SIZE OF CHARGE											4	
RATE OF CHARGING											5	
TIME ACTUALLY MIXING		CONTIN. DUTY			INTERMIT. DUTY						6	
TYPE OF MIXING (turbulent/moderate/light)											7	
SOLIDS CONTENT		SOLIDS S.G.									8	
LIQUID VISCOSITY		LIQUIDS S.G.									9	
SLURRY VISCOSITY (APPARENT)											10	
PARTICLE SIZE ANALYSIS											11	
SOLIDS SETTLING VELOCITY											12	
											13	
<b>Vessel Data</b>											14	
DEPTH OF VESSEL											15	
DEPTH OF LIQUID		MAX			NORMAL			MIN			16	
ANGLE OF AGITATOR											17	
SIZE OF APERTURE FOR IMPELLER											18	
WORKING PRESSURE											19	
WORKING TEMPERATURE											20	
DEPTH OF VESSEL											21	
											22	
<b>Technical Data</b>											23	
TYPE OF MIXER											24	
No. OF BLADES		DRAWING No.									25	
No. OF SETS OF BLADES		ELECTRICITY SUPPLY			Volts		phase		Hz		26	
SPEED											27	
SHAFT DIAMETER											28	
CRITICAL SPEED											29	
TYPE OF SEAL OR GLAND		RECOMMENDED MOTOR POWER (hp/kW)									30	
METHOD OF SUPPORT		RECOMMENDED MOTOR SPEED (rpm)									31	
TOTAL LOAD											32	
WITHDRAWAL HEIGHT REQUIRED		INERTIA									33	
TYPE OF BEARINGS		STARTING TORQUE									34	
ANGLE OF BLADES		OPERATING TORQUE									35	
		TYPE OF GEAR BOX									36	
		VEE BELT/DIRECT DRIVE									37	
<b>Design Standards and Inspection</b>											38	
DESIGN CODE		MAX. ERECTION WEIGHT									39	
HYDROSTATIC TEST PRESSURE		SHIPPING WEIGHT									40	
DRGS and DATA REQ.		SHIPPING VOLUME									41	
INSPECTION		TOTAL WEIGHT									42	
<b>Materials of construction</b>											43	
SHAFT		IMPELLER									44	
SUPPORTS											45	
VESSEL		SEAL OR GLANDS									46	
BEARINGS											47	
											48	
DATE OF ENQUIRY		DATE OF ORDER									49	
DRG. No.		ORDER No.									50	
MANUFACTURER											51	
<b>REMARKS</b>											52	
											53	
											54	
											55	
											56	
											57	
Prepared		3			6						58	
Checked		2			5						59	
Approved		1			4						60	
Date		Engineering			Process			REV		By		61
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Equipment No.											64	
Project No.											65	

<p style="font-size: 1.2em; margin: 0;">Conveyor data sheet</p> <p style="margin: 0;">(PROCEED)</p>								Equipment No. (Tag)				
								Descript. (Func.)				
								Sheet No.				
Operating Data												1
												2
No. REQUIRED			OVERALL LENGTH									3
HOPPER WIDTH			WEIGHT UNLADEN									4
			WEIGHT LADEN									5
CONVEYOR TYPE			WIDTH									6
CONVEYOR LENGTH HORZ. SECTN			ELEVATED SECTION									7
BUCKET TYPE			SPACING									8
BELT SPEED			VARIABLE/RXED									9
BELT TENSION			DRIVE									10
POWER CONSUMPTION			POWER SUPPLY									11
Safety Characteristics												12
												13
MATERIAL TO BE CONVEYED												14
MASS FLOW RATE												15
BULK DENSITY												16
MATERIAL OF CONSTRUCTION												17
BELT			BEARING TYPE									18
HOPPER												19
BUCKET			BEARING SPACING									20
												21
DATE OF ENQUIRY			DATE OF ORDER									22
DRG. No.			ORDER No.									23
MANUFACTURER												24
												25
SPECIAL CHARACTERISTICS												26
												27
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												57
Prepared				3				6				58
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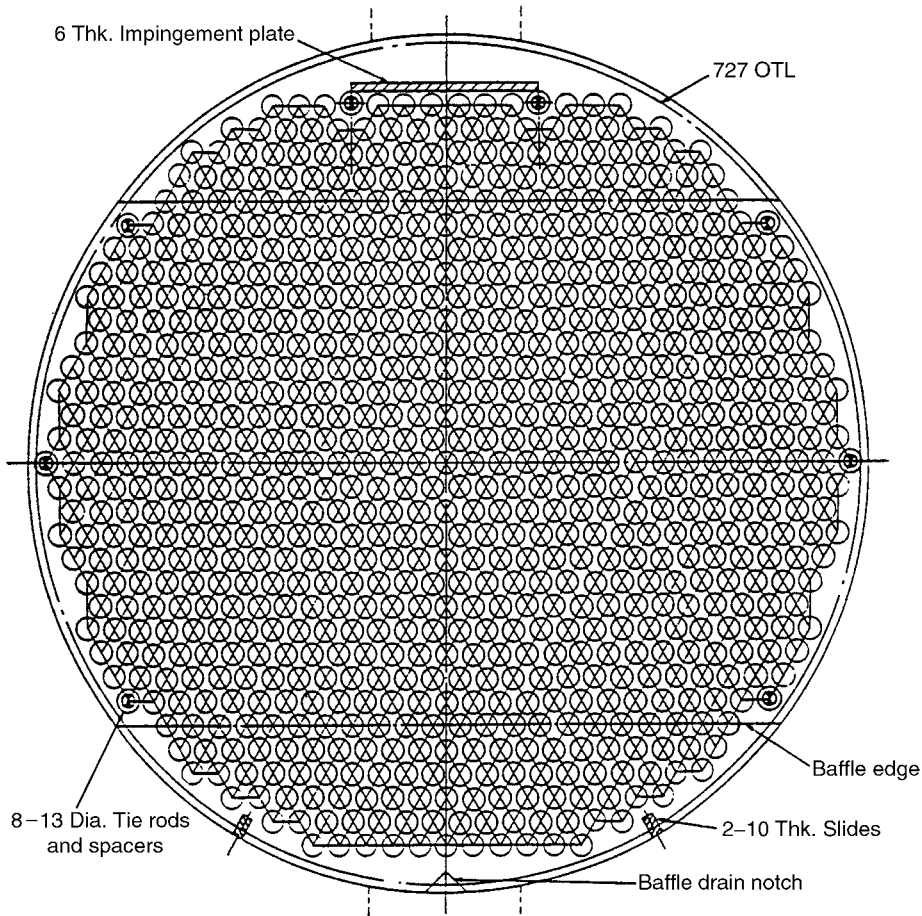


APPENDIX H

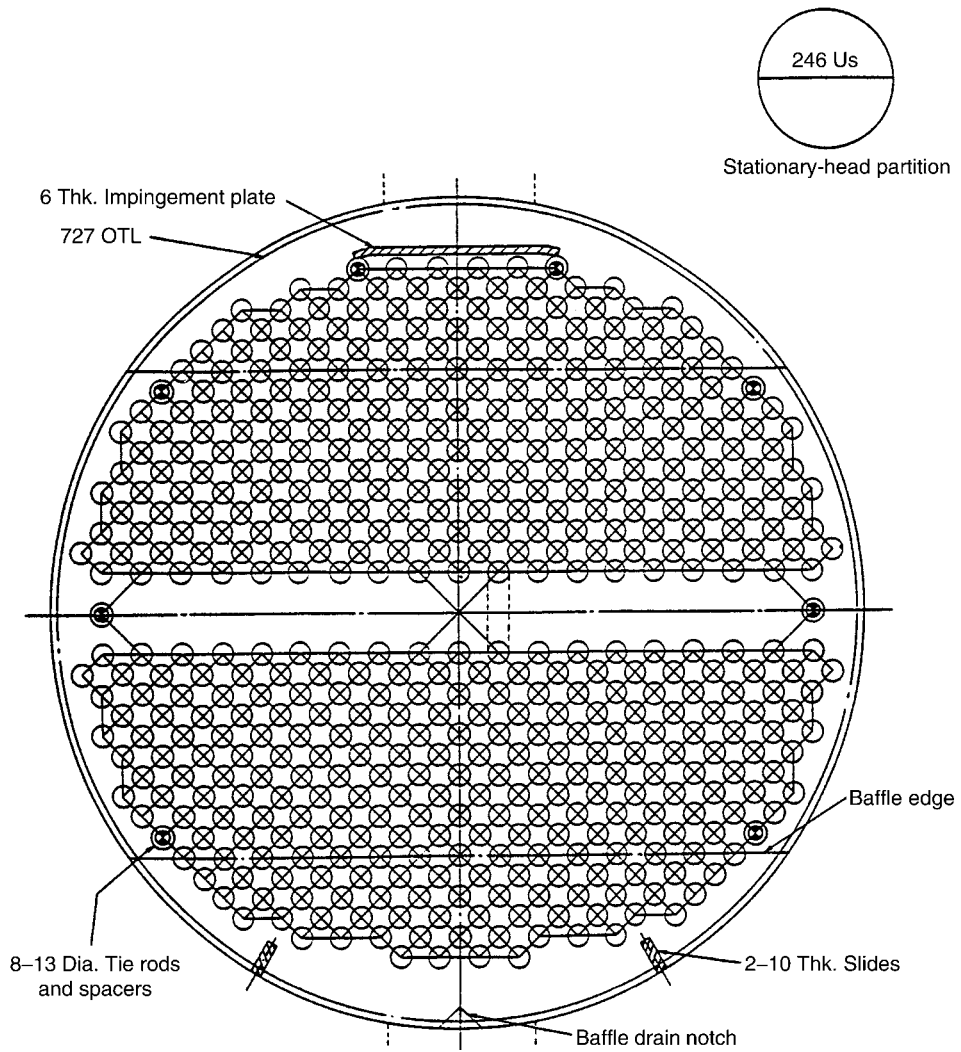
*Typical Shell and Tube Heat Exchanger  
Tube-sheet Layouts*

- (a) Fixed tube-sheet exchanger
- (b) U-tube exchanger
- (c) Floating-head exchanger with split backing ring
- (d) Pull through floating-head exchanger

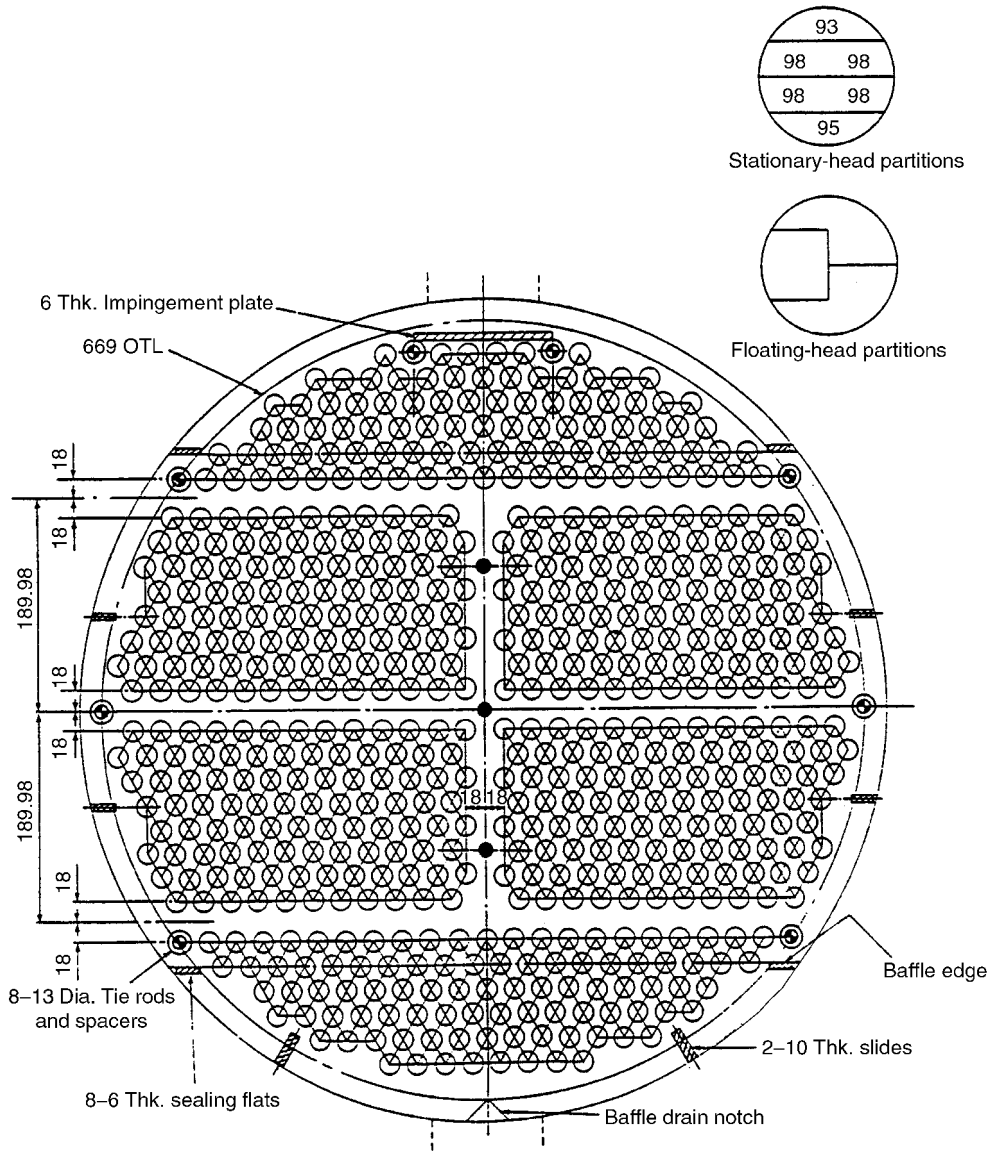
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(a) Typical tube layout for a fixed tubesheet exchanger 740 i/Dia. shell, single pass, 780-tubes, 19.05 o/Dia. on 23.8125 pitch, 30° angle.

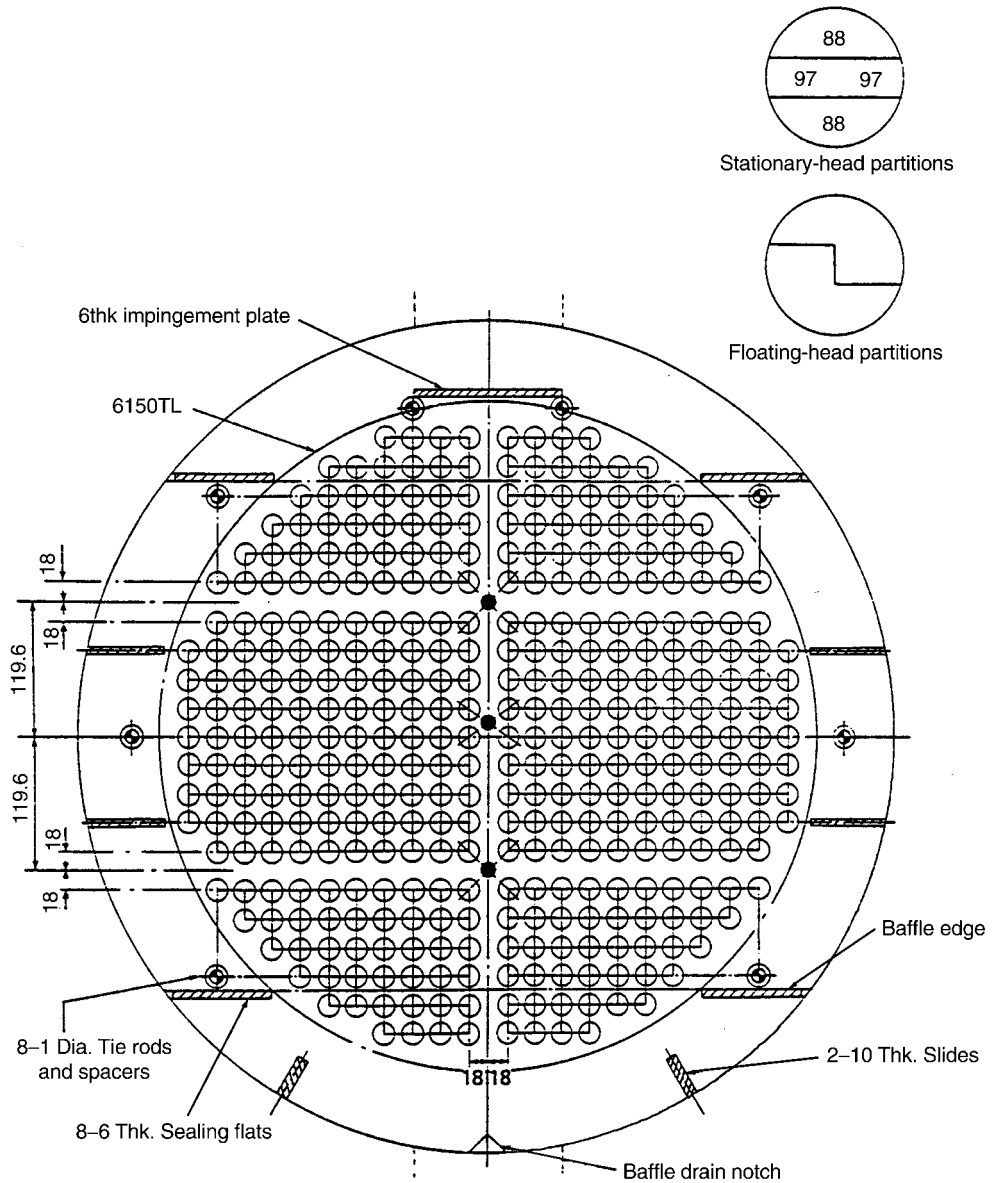


(b) Typical tube layout for a U-tube exchanger 740 i/Dia. shell, 2-pass, 246 U-tubes, 19.05 o/Dia. on 25.4 pitch, 45° angle.



(c) Typical tube layout for a split backing ring floating-head exchanger. 740 i/Dia. shell, 6-pass, 580 tubes, 19.05 o/Dia. on 25.4 pitch, 30° angle.

• Denotes 13 Dia. sealing bars.



(d) Typical tube layout for a pull-through floating-head exchanger. 740 i/Dia. shell, 4-pass, 370 tubes 19.05 o/Dia. on 25.4 pitch, 90° angle.

• Denotes 13 Dia. sealing bars.

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