Fundamentals *of* Equilibrium and Steady-State Thermodynamics

by

Nicholas W. Tschoegl

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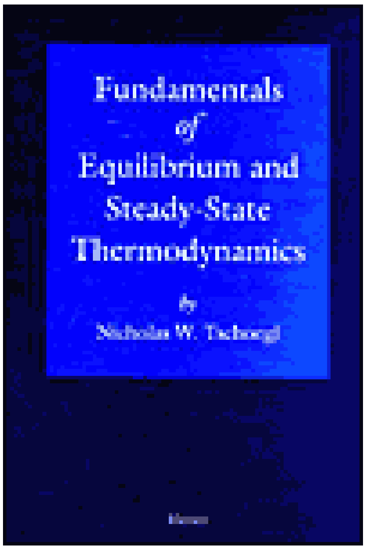

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PREFACE

> "The history of modern science has shown repeatedly that a quantitative description of nature can often be achieved most successfully by first idealizing natural phenomena, i.e., by setting up a simplified model, either physical or mathematical, which crudely describes the essential behavior while neglecting details. – The behavior of nature is then related to the idealized model by various correction terms which can be interpreted physically and which sometimes can be related quantitatively to those details in nature which were neglected in the process of idealization."
>
> J. M. Prausnitz

This book contains essentially the somewhat expanded material of a one-term course which I presented at the California Institute of Technology over several years. In that course I attempted to summarize the salient features of both equilibrium and steady-state thermodynamic theory under a *uniform postulatory viewpoint*. I wished to emphasize the *logical structure* of thermodynamic theory, its *formal aspects*, to allow it to emerge as a coherent whole, unfettered by much of those details which—albeit indispensable in practical applications—tend to obscure this coherent structure. Largely because of this, I also avoided any statistical mechanics or reference to molecular structure—barring an occasional allusion. The treatment is, therefore, 'classical', or—using a perhaps more appropriate word—'phenomenological'. Thus the concept of entropy (as is that of chemical potential) is introduced simply as required by the formalism—to complete the pattern, as it were.

I almost exclusively dealt with 'ideal' systems. I made an exception (the van der Waals equation of state) only when discussing phase transitions because ideal gases do not show such transitions. Generally, I took the view that the treatment of 'real' systems properly belongs into the realm of *applied*, rather then *theoretical thermodynamics*. For these reasons, only *selected ideal systems* are covered. *Ideal gases* are discussed extensively. The *ideal solution* is treated as an example of a liquid system. The *amorphous ideal rubber* serves as an example of a solid. I chose this partly because much of my research has been concerned with the properties of rubberlike materials, but—perhaps more importantly—because the formalism developed is a model for the treatment of other, non-simple systems. To avoid getting into lengthy discussions that—in my opinion—contribute nothing essential to an exposition of the fundamental structure of thermodynamic theory, I did not talk about crystalline solids. I also omitted dealing with critical phenomena in terms of scaling laws. I do not consider these omissions to be shortcomings of the text as I concentrated on conveying a sense of the structure of the theory.

J. M. Prausnitz's (1978) words in the motto refer to ideal systems. They apply equally well, however, to the whole approach I took in the course. The theory I presented is an idealized *model* theory designed to help us understand thermodynamics. Any such model, if correctly developed, stands on its own as a creation of the human mind whether it applies or not to anything in nature. In fact, the simplifying assumptions that must be made when constructing such a model virtually guarantee that it *cannot* truly describe reality. Its usefulness lies in the fact that it is relatively easy to grasp, that it orients our thinking, and that we can 'get away' with trying to apply it to reality because its *domain of validity* can come arbitrarily close to reality. One can 'get away' with it only within this domain which must be defined and appreciated. The ideal gas furnishes a perfect illustration of this point. It is the essence of a model that it can never truly be in a one-to-one correspondence with reality, not even within its domain of validity. To construct a perfect model one would have to be the Creator Himself.

The course was not meant to be a first course in thermodynamics. It was presented to classes consisting mainly of chemical engineering, materials science, and chemistry graduate students with a smattering of undergraduates. All students had had undergraduate thermodynamics and many had some other graduate thermodynamics courses. Nevertheless, in unsigned but obligatory course evaluations the students asserted that they found the course helpful and that they liked it because it presented the material in a novel way.

I was struck by my students' almost uniform clamor for *more* steady-state thermodynamics. None of them had been exposed to steady-state theory before. They were clearly intrigued by it and felt (as do I) that a knowledge of at least the rudiments of steady-state theory deepens the understanding of thermodynamics as a whole, and that it guides one's thinking in this field. It does seem useful to me to discover that such well-known empirical relations as Fourier's Law of Heat Conduction and Fick's First Law of Diffusion can be firmly founded in steady-state theory. In particular, I deem it most gratifying to learn that the steady state is a state of minimum entropy production. My own, perhaps novel, contribution consists in paralleling the notions—central to the exposition of equilibrium thermodynamics in this text—of *entropy and energy representations* by the notions of *entropy production and energy retention representations* in my treatment of the theory of coupled linear steady states. In view of my students' interest in the thermodynamics of the steady state, I was tempted to enlarge this part of the book. I eventually decided against it because I felt that whetting the readers appetite is all I really am qualified to do.

The exposition is *postulatory*, i.e., it is based on a small number of *postulates* which are simply assumed to be valid without further justification. Their ultimate justification must be sought in their usefulness. The arguments in favor of a postulatory exposition have been well presented by H. Callen (1963, 1985). In my lectures I pointed out that—stretching an analogy—postulates somewhat resemble base vectors. One simply defines an appropriate set of base vectors to suit one's purpose. It is the same with postulates. I emphasized that currently there does not appear to be any way to decide how many postulates are required to completely underpin the theory, and that there are at this time no rigorous methods to decide whether a given set of postulates is complete.

These and other difficulties with thermodynamics as a physical science arise from its non-metric character. Weinhold (1975, 1976) has introduced a 'metric' into thermodynamics. This work has attracted less attention than it probably deserves, partly perhaps because the mathematics are couched in the 'language' of Dirac's *ket* and *bra* notation which is familiar to quantum physicists but not to the majority of thermodynamicists. To me Weinhold's metric thermodynamics—although intriguing—did not appear to make the presentation of thermodynamic theory any easier and so I did not include it in my lectures.

Callen (1974, 1985) pointed out that the non-metric nature of thermodynamics implies that it is rooted in symmetry relations rather than quantitative laws. He then proceeded to outline the role of symmetry considerations in thermodynamics, effectively basing thermodynamics on symmetry laws. This is certainly promising work. However, it has apparently not yet led to predictions concerning the nature, number, and role of postulates in the theory.

The book is subdivided into three parts. These are:

I. Equilibrium Thermodynamics
II. Steady-state Thermodynamics
III. Appendices.

The text is followed by a list of references, a list of symbols, and a quite detailed author and subject index. The first Part contains twenty-one chapters, the second nine. There are seven appendices. The chapters are broken down into sections, each with its own number and title. The former serve for indexing and cross-referencing. I tried to keep these sections quite short and concise. Thus, some contain just a paragraph or two. Others that could not be subdivided profitably are somewhat longer. A section entitled "Chapter Contents" lists them at the beginning of each chapter.

A word needs to be said about the figures in the text which depict the fundamental surface in thermodynamic configuration space (Figs. 3-2, 4-3, 4-4, 5-1, and 5-4). I followed Callen (1963, 1985) in their representation, adapting them slightly for my own purposes. These figures are essentially streamlined versions of J. C. Maxwell's plaster model of the thermodynamic surface of water, which he presented to Gibbs in 1875 (Weinhold, 1978).

Finally, the mottoes on the title pages of the three parts of the book and at its end are from Arthur Whaley's (1938) translation of the *Analects of Confucius*. The first is from Book II-17, the second from Book IX-16, the third from Book I-1, and the fourth from Book VII-1, 2, 3.

Naturally, I did not invent any new thermodynamics. Rather, this book is an amalgam, or distillate, of ideas culled from a number of excellent textbooks, notably Callen (1963, 1985), but also Abbott and van Ness (1972), Blinder (1969), Kestin (1966), Modell and Reid (1983), Denbigh (1965, 1966), ter Haar and Wergeland (1966), Zemansky (1968), de Groot and Mazur (1984), Haase (1966), Prigogine (1967), Wisniewski *et al.* (1976), and others more. I hope that this short 'structural overview' will find favor with students, teachers, and engineers. I would greatly welcome any feedback, including references to typographical or other errors.

In conclusion, it is a pleasure to acknowledge the helpful suggestions I received from two of my colleagues, Zhen-Gang Wang and Constantinos Giapis. The latter, in particular, read the entire manuscript. I deeply appreciate their efforts. I am also indebted to Igor Emri of the University of Ljubljana for his most welcome comments and suggestions.

CONTENTS

I. EQUILIBRIUM THERMODYNAMICS

II. STEADY-STATE THERMODYNAMICS

III. APPENDICES

1. DEFINITIONS

This text presents the fundamentals of the structure of the phenomenological theory of equilibrium and steady-state thermodynamics on a *postulatory basis*. A postulatory basis is a set of independent statements, serving as the necessary and sufficient foundation of a deductive system of thought.

This chapter contains a glossary of certain essential conceptual tools of equilibrium and steady-state thermodynamics that simply require some comment (e.g., *energy, matter, work,* etc.) or, at best, a dictionary definition to establish their meaning with some precision (e.g., *system, state, process,* etc.). Others will need some understanding of the theory and will be defined in the text.

All of these concepts are required in the development of the theory but are not part of the postulatory basis. Many, if not all, may not have real physical existence. However, they can always be imagined to result from an extension of some quality or property to an appropriate limit.

1.0 Chapter Contents

1.1 Energy and Matter

Energy and matter are the two fundamental manifestations of physical reality. They are interconvertible; however, this interconvertibility will not play any role in this text. We will primarily be concerned with *energy* interchanges. *Matter* will enter our considerations largely because changes in the amount of matter or in its composition are generally accompanied by exchanges of energy.

1.2 Thermodynamics

Thermodynamics is the science of heat as a special form of energy exchange. It is thus a branch of *energetics*, the general science of the forms and interchanges of energy. From a thermodynamic standpoint energy can be exchanged in two fundamental ways: in the form of *work* or in the form of *heat*. Work or heat represent energy transfers. They are energy in transit.

Thermodynamics may conveniently be subdivided into two main disciplines: equilibrium and non-equilibrium thermodynamics. *Equilibrium thermodynamics* deals with the thermodynamics of systems in mechanical, chemical, and thermal equilibrium and is treated in Part I of this text. *Non-equilibrium thermodynamics* is the thermodynamics of irreversible processes. It can be further subdivided into *steady-state thermodynamics,* treated in Part II of this text, and non-steady-state or general, *irreversible thermodynamics* that is outside the scope of this text.

1.3 Theoretical and Applied Thermodynamics

There are two sides to every body of knowledge: a theoretical and a practical side. The theoretical side is concerned with the codification, in a self-contained and self-consistent manner, of the principles and rules that govern that particular field of knowledge. The practical side is concerned with the application of those principles and rules to reality. As in any science, in any thermodynamic discipline we also distinguish these two sides, namely, theoretical and applied thermodynamics. This text deals with the former.

1.4 Work, Heat, and Energy

Work is transfer of energy to the macroscopically *observable* coordinates of motion of the constituents of matter. In the performance of *physical work* the material composition remains unchanged. Examples of physical work are mechanical, electrical, and magnetic work.

In contradistinction to physical work *chemical work* is associated with changes in (internal) energy resulting from changes in the amount or the chemical composition of matter. Since its nature is quite different from that of physical work (it cannot be measured in any *direct* way), the term *mass action* is preferable and will be used throughout this text where the distinction appears indicated. Occasionally both physical *and* chemical work will be subsumed under the common term of work.

Heat is transfer of energy to the macroscopically *unobservable* (or *hidden*) coordinates of motion.

Energy manifests itself as work or heat when crossing the boundaries of a system. It is diminished, when work is done, by an amount equal to the work and is therefore defined in terms of work and expressed in the same units. *Potential energy* is the capacity for mechanical work that a body possesses by virtue of its position. *Kinetic energy* is the capacity for mechanical work that a body possesses by virtue of its motion. The concepts of potential and kinetic energy are useful also in considering forms of energy other than mechanical. Potential and kinetic energy are referred to as *external energies*. *Internal energy* will be introduced later in the text.

1.5 Factorability of the Energy

Any form of energy exchange can always be expressed as the product of two factors or parameters: an *intensity factor or intensive parameter*, and a *capacity factor* or *extensive parameter*. The capacity factor depends on the extent or the amount of the system under consideration. The intensity factor does not. It is the same in any part of the system regardless of its size. As two examples, if the energy exchange is in the form of pressure-volume work, then the intensity factor is the pressure, and the capacity factor is the volume;

if it is in the form of electrical work, then the former is the voltage, and the latter is the charge.

1.6 Ideal and Real Thermodynamic Systems

A thermodynamic system is that part of the physical universe which has been singled out for observation or manipulation. An *ideal thermodynamic system* is a *model system* whose behavior underlies the behavior of a corresponding *real system.* As a model system, the ideal system is a simplification which allows it to be subjected to a rigorous treatment within the compass of *theoretical thermodynamics.* The behavior of idealized model systems simulates the behavior of real systems under certain limiting conditions. The thermodynamic treatment of real systems—though important—does not, however, contain anything new in a fundamental theoretical sense and, therefore, belongs in the realm of *applied thermodynamics.*

1.7 Thermodynamic Systems and their Surroundings

That part of the physical universe with which a given thermodynamic system may interact is called the *environment*, or the *surroundings*, of the system. The means by which the system is separated from its surroundings are called its *boundaries*. The boundaries of a system are also referred to as *barriers, constraints, restraints*, or *walls.*

With respect to their interaction with their surroundings we distinguish several thermodynamic systems. A system which exchanges neither matter nor energy with its surroundings is an *isolated system.* A system that does not exchange matter with its surroundings but may exchange energy with it is called a *closed* system. The boundary of a closed system is *impermeable*, i.e., it is restrictive with respect to matter.

A system which exchanges both matter and energy with its surroundings is an *open* system. The boundary of an open system is *non-restrictive* with respect to matter. It is *permeable* when it is non-restrictive to all forms of matter, and *semi-permeable* when it is non-restrictive to some form of matter but restrictive to all other forms. With respect to energy interchanges, the walls of an open system are *movable* or *rigid* according to whether they permit exchange of energy in the form of *physical work* or do not; and they are called *diathermal* or *adiabatic* according to whether they permit exchange of energy in the form of *heat* or do not.

1.8 Reactive and Non-Reactive Systems

A system in which chemical or nuclear reactions are allowed to occur is a *reactive* system. In the absence of chemical or nuclear reactions the system is *non-reactive*. This text deals with isolated reactive chemical systems only.

1.9 Simple Thermodynamic Systems

The thermodynamic system with which this text will mainly be concerned is referred to as a *simple system.* A *simple thermodynamic system* is, by definition, macroscopically homogeneous, isotropic, uncharged, chemically inert (non–reactive), and is sufficiently large so that surface effects can be neglected. It is not acted upon by electric, magnetic, or gravitational fields. Pressure is the only mechanical force allowed to affect the simple system. A simple system thus only undergoes dilation or contraction.

A *single-component simple system* contains only one kind of matter. A *multicomponent simple system* contains two or more kinds of matter. A simple system with constant composition will be called a *physical simple system.*

A *composite (simple) system* comprises at least two simple systems, divided by a controllable internal barrier which is restrictive to at least one form of energy or matter. It is often convenient to consider the system of interest and the surroundings with which it interacts as two subsystems combined into an isolated composite system.

A *non-simple system* is a system which is not bound by the criteria applicable to a simple system.

1.10 Thermodynamic Properties

The macroscopic observables which survive statistical averaging over the microscopic coordinates of motion are called *thermodynamic properties, coordinates, variables,* or *parameters.* A thermodynamic property is a variable whose change during any change of state depends only on the initial and final state of the system. It is, therefore, also called a *variable of state* or *function of state.* An infinitesimal change in a state variable is an *exact differential* (see Appendix 1).

Properties are measurable either directly (*primitive properties,* e.g., volume, pressure, or temperature) or indirectly (*derived properties,* e.g., internal energy, entropy, or chemical potential). Properties are *neutral properties* if they play no role in the energy exchange considered (e.g., color).

A property is *extensive* if it depends on extent (length, area, volume) or on amount (mass, charge). A property is *intensive* if it does not depend on extent or amount. A property may be neither extensive nor intensive. An extensive property becomes intensive when scaled with respect to either extent or amount. An extensive property becomes a *molar property* when expressed per mole of matter, a *specific property* when expressed per unit of mass, and a *density* when expressed per unit volume. Molar and specific properties are intensive and so are densities.

1.11 Thermodynamic Equilibrium

The concept of equilibrium is taken from mechanics but is basic in thermodynamics as well. We distinguish between stable, metastable, unstable, and neutral equilibrium. When a thermodynamic system is in *stable equilibrium,* a perturbation will result only in small (virtual) departures from its original conditions and these will be restored upon removal of the cause of the perturbation. A thermodynamic system is in *unstable equilibrium* if even a small perturbation will result in large, irreversible changes in its conditions. A system in metastable equilibrium will act as one in stable equilibrium if perturbed by a small perturbation but will not return to its initial conditions upon a large perturbation. Finally, a system in neutral equilibrium will not suffer any change in its conditions under any perturbation.

1.12 Thermodynamic States

The state of a thermodynamic system is its condition as specified by its properties. For any system there is a minimum number of properties which completely characterize its state.

A system is in a state of (stable) *thermodynamic equilibrium* if its state can be described by properties which do not depend on time and are the same at any point of the interior of the system. A system in a state of equilibrium does not interact with its environment. A *simple system* is in a state of equilibrium when it is in mechanical, chemical, and thermal equilibrium.

A system which exchanges energy and/or matter with its environment at a constant rate is said to be in a *stationary* or *steady state*. The properties of a system in a steady state are also time-invariant but are generally different at different points of its interior.

1.13 Thermodynamic Processes

A change from one equilibrium state to another is called a *change of state* or a *process*. An infinitesimal change that may or may not take place but is compatible with the constraints of the system is called a *virtual change*.

A process that is carried out at an infinitely slow rate so that it is at all times infinitesimally close to a state of thermodynamic equilibrium is called a *quasistatic* ('almost static') *process*. A quasistatic process is thus an ordered succession of equilibrium states.

A *reversible process* is conducted in such a manner that, at its conclusion, both the system and its surroundings are restored to their initial state without producing a change in the rest of the universe. A reversible process is necessarily quasistatic.

A *real physical process* (a *spontaneous natural process* or *actual process)* is a temporal evolution of equilibrium and non-equilibrium states. Such a process is *irreversible*.

A *cyclic process* is a process in which the system is returned to its initial state after completion of the cycle.

1.14 Thermodynamic Functions

Thermodynamic functions are either *state functions* or *process functions*. A state function (or function of state) is independent of the process by which the final state is reached from the initial state and thus depends solely on the initial and final state of the system. By contrast, a process function depends on the way by which the final state is reached from the initial one. The differential of a state function is an *exact*, that of a process function an *inexact differential*. Appendix 1 contrasts exact and inexact differentials.

1.15 Postulates, Laws, Principles, Rules, and Theorems

In this text there are frequent references to postulates, laws, principles, rules, and theorems. These terms are largely traditional and the distinction between their meanings is often somewhat tenuous. In general:

Postulates are propositions to be accepted without proof. They form the first premises in trains of thought and are commonly (as in this text) referred to under a descriptive name or phrase (e.g., the Postulate of the Existence of Entropy). By contrast, laws, principles, rules, and theorems are usually associated with a personal name (e.g., Henry's Law, Le Châtelier's Principle, Maxwell's Rule, the Gibbs Theorems) but there are exceptions (e.g., the Second Law of Thermodynamics, the Principle of the Conservation of Energy, etc.).

Laws are formal statements of the manner or order in which a set of natural phenomena occur under certain conditions. These phenomena are, as far as is known, invariable under the stated conditions.

Principles enunciate an established mode of action or operation in natural phenomena. Principles emphasize the idea of fundamental truth or general applicability.

Rules are prescribed forms, methods, or sets of instruction for solving a given class of problems. Rules emphasize the idea of more specific direction or regulation.

Theorems are general statements that have been proved or whose truth has been conjectured. They embody that which has been considered and established as a principle or law; hence, sometimes, a rule.

2. THE POSTULATES OF EQUILIBRIUM THERMODYNAMICS

A thermodynamic system is characterized in terms of its *extensive* properties. In addition to the directly measurable extensive parameters such as the volume, V, or the mole number, N, complete characterization requires two additional extensive thermodynamic parameters, the *internal energy*, U, and the *entropy*, S. These are not measurable directly and are introduced through postulates. Three additional postulates complete the postulatory basis upon which the discussion of equilibrium thermodynamics in this text is based.

2.0 Chapter Contents

2.1 Existence of an Internal Energy – POSTULATE I

Postulate I asserts that:

> *"For any thermodynamic system there exists a continuous, differentiable, single-valued, first-order homogeneous function of the extensive parameters of the system, called the internal energy, U, which is defined for all equilibrium states".*

2.2 Additivity of the Internal Energy

Being a function of the extensive parameters of the system, the internal energy is itself extensive and is therefore additive over the subsystems of a composite system.

2.3 Path Independence of the Internal Energy

Being defined for all equilibrium states, the internal energy is a function of state or *state function* (§ 1.14). A change in internal energy therefore depends solely on the difference between the values of U in the final and initial states and is independent of the path along which the system has been led between these states. A finite change, ΔU, is thus given by

$$\Delta U = \int_{U_\mathrm{i}}^{U_\mathrm{f}} dU = U_\mathrm{f} - U_\mathrm{i} \tag{2.3}$$

where the subscripts f and i refer to the final and initial states, respectively. It further follows that dU, an infinitesimal change in U, is an *exact differential* (see Appendix 1).

2.4 Conservation of the Internal Energy – POSTULATE II

Postulate II claims that:

> *"In an isolated composite system the total change in internal energy over all subsystems involved in the change is zero."*

Mathematically this is expressed by the relation

$$\Delta U_\mathrm{Total} = 0. \tag{2.4}$$

Postulate II asserts the conservation of energy. According to this postulate, in an isolated system energy can neither be destroyed nor created. Clausius (1850) stated this in the words: *'Die Energie der Welt ist konstant' (The energy of the universe is constant).*

2.5 Internal Energy Transfer: Work, Mass Action, and Heat

Equilibrium thermodynamics is concerned with the transfer, or exchange, of energy in quasistatic processes. In this text energy transferred *to* the system is *positive,* and energy transferred *from* the system is *negative*

Work is the change in the internal energy of a non-reactive thermodynamic system resulting from the performance of physical work either on or by the system while it is isolated from its surroundings by adiabatic impermeable walls.

Mass action manifests itself in two distinct ways in a thermodynamic system. In an *open system* it is the change in internal energy resulting from a transfer of matter into or out of the system while it is enclosed by adiabatic rigid walls. In a *closed system* it is the change in internal energy resulting from a change in the composition of matter while the system is confined between adiabatic, rigid, and impermeable walls.

Heat is the change in the internal energy of a non-reactive thermodynamic system resulting from the transfer of energy to or from the system in a quasistatic process while the system is isolated from its surroundings by rigid impermeable walls.

Work, mass action, and heat are *not* functions of state. Because they are *process functions* (cf. § 1.14), elemental changes in these quantities are *inexact differentials* We denote an inexact differential by δ instead of d (see Appendix 1).

2.6 Heat as a Form of Energy Exchange—The First Law of Thermodynamics

An increase in the internal energy, ΔU, of a system, not in motion, is equal to the energy transferred to it in the form of (physical) work, W, mass action, M, or heat, Q. A finite change in U is therefore given by

$$\Delta U = W + M + Q\,, \tag{2.6$_1$}$$

while an elemental change becomes

$$dU = \delta W + \delta M + \delta Q\,. \tag{2.6$_2$}$$

Equations (2.6) represent the *principle of the conservation of energy* in thermodynamics. They extend the scope of the principle as formulated in mechanics to include heat as a form of energy transfer and are commonly considered to constitute mathematical expressions of the *First Law of Thermodynamics* (cf. § 7.16).

The equations clarify the meaning of *path* in § 2.3 and, hence, the meaning of the term *process function* and *function of state* (§ 1.14) The same change in internal energy will result if the change in any of the quantities W, M, Q, or δW, δM, δQ, is exactly compensated by an equivalent change in either or both of the other two. Since the way in which this can be achieved is arbitrary, a final state can be reached from a given initial state along a variety of paths.

2.7 Heat Exchanged with the Surroundings and Internally Generated Heat

Apart from heat, Q, that is imparted to, or is abstracted from, the system, i.e., the heat *exchanged* between the system and its surroundings, there is another form of heat, Q', that is not transferred into or out of the system but is generated in its interior as a result of the unavoidable energy dissipation in real physical, i.e., irreversible, processes.

Clausius (1850) who introduced the concept, called Q' the 'uncompensated heat' because it is not 'compensated' for in the surroundings of the system by a commensurate change in heat. It would more fittingly be called 'heat generated irreversibly in the interior of the system'. Since this expression is too unwieldy, we shall call it simply the *internally generated* heat. This heat is always produced at a finite rate and, hence, is not quasistatic. It is always positive and vanishes only in reversible processes (cf. Chapter 5). In the thermodynamics of irreversible processes an attempt is made to determine it quantitatively (cf. Part II). In equilibrium thermodynamics it plays only a subordinate qualitative role.

2.8 Measurability of Changes in Internal Energy

The internal energy, U, cannot be measured directly. However, only *changes* in internal energy are of concern in thermodynamics and these changes can be measured by physical means. The measurability of changes in internal energy follows from Eq. (2.6)$_1$ and, hence, ultimately from Postulate II upon which the equation rests. For a non-reactive thermodynamic system of constant composition, enclosed by an adiabatic, impermeable wall, Eq. (2.6)$_1$ reduces to $\Delta U = W$. Now, the physical work, W, can be measured by physical means and, given two equilibrium states, A and B, it is always possible to carry the system either from state A to state B, or from state B to state A, by some physical process while the system is enclosed by adiabatic impermeable walls (Joule 1847, 1849). Hence,

ΔU can be determined by measuring the work, W, done in the process under the stated conditions.

2.9 Measurability of the Heat Flux

By Eq.(2.6)$_1$, in any process, the heat flux[1] to or from a system enclosed by impermeable walls is equal to the change in internal energy diminished by any work done in the process. Since both ΔU and W can be measured, so then can Q. A device which measures heat fluxes is called a *calorimeter*. The heat evolved or absorbed in a system undergoing chemical reactions can also be determined calorimetrically (cf. § 21.6).

2.10 Measurability of the Mass Action

In a *closed system* mass action results from a change in composition within an isolated system. Since the system is isolated, $\Delta U = 0$, and, by Eq.(2.6)$_1$ the mass action term becomes

$$M = -W - Q\,. \tag{2.10}$$

If volume change is the only work, this can be determined, and the heat can be measured in a calorimeter. If volume change is not the only work, the mass action can still be measured in principle although it may be difficult to devise a suitable experimental arrangement.

The mass action representing the change in internal energy resulting from a flow of matter either to or from an *open system* is quite another matter. The flow of matter is an inherently irreversible process. Matter always transports with it a certain amount of energy. In isothermal diffusion in the steady state the energy transported per mole of matter, the so-called *energy of transport*, may be obtained, at least in principle, from measurements of the *heat of transport* if the molar enthalpy of the fluid is known. A fuller discussion of this topic must, however, be deferred until the concepts of the energy of transport and the heat of transport have been properly introduced in Part II. It will be taken up again in § 29.5.

2.11 Infinitesimal Change in Work

When only rigid barriers are lifted in a composite system, the infinitesimal change in internal energy equals the infinitesimal change in work and is given by

$$dU = \delta W = \sum\nolimits_k \left.\frac{\partial U}{\partial X_k}\right|_{X(\neq X_k)} dX_k \qquad (k = 1, 2, \ldots, r) \tag{2.11}$$

where the X_k are the extensive primitive (i.e., observable or measurable) parameters of the system *excluding the mole numbers*, and X denotes the totality of all extensive parameters.

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[1] The terms `heat' and `heat flux' may generally be used interchangeably.

2.12 Infinitesimal Change in Mass Action

When only impermeable barriers are lifted in a non-reactive composite system, the infinitesimal change in internal energy equals the infinitesimal change in mass action and is given by

$$dU = \delta M = \sum\nolimits_k \frac{\partial U}{\partial X_k}\bigg|_{X(\neq N_k)} dN_k \qquad (k = \mathrm{r}+1, 2, \dots) \qquad (2.12)$$

where the N_k are the *k*th mole numbers and X is again the totality of all extensive parameters.

2.13 Insufficiency of the Primitive Extensive Parameters

The primitive, i.e., the directly measurable, extensive parameters, X_k, of a thermodynamic system are insufficient to determine the infinitesimal change in internal energy when an adiabatic constraint is lifted, because none of them is an extensive parameter of heat.

Temperature is the *intensive* parameter of heat. The recognition that energy can always be factored into the product of an extensive and an intensive parameter (cf. § 1.5) allows us to introduce the required *extensive* parameter of heat simply through a postulate.

2.14 Existence of Entropy – POSTULATE III

Postulate III states that:

> *"For any thermodynamic system there exists a continuous, differentiable, single-valued, first-order homogeneous function of the extensive parameters of the system, called the entropy, S, which is defined for all equilibrium states and which is the extensive parameter of heat."*

2.15 Additivity of the Entropy

Being a function of the extensive parameters of the system, the entropy is itself extensive and is therefore additive over the subsystems of a composite system.

2.16 Path Independence of the Entropy

Being defined for all equilibrium states, the entropy is a state function. A change in entropy therefore depends solely on the difference between the values of S in the final and initial states and is independent of the path along which the system has been led between these states. A finite change, ΔS, is therefore given by

$$\Delta S = \int_{S_\mathrm{i}}^{S_\mathrm{f}} dS = S_\mathrm{f} - S_\mathrm{i} \qquad (2.16)$$

where the subscripts f and i again refer to the final and initial states. It follows further that dS, an infinitesimal change in S, is an *exact differential* (see Appendix 1).

2.17 Non-Conservation of Entropy – POSTULATE IV

In contrast to the internal energy, entropy is not conserved. Postulate IV asserts that:

> *"In a closed adiabatically isolated system the change in entropy over all subsystems involved in the change is positive semi-definite".*

Mathematically this may be expressed by the relation

$$\Delta S_{\mathrm{Total}} \geq 0\,. \tag{2.17}$$

The change is zero only in a reversible process. In any real physical process (or spontaneous natural process) the change is positive. Equation (2.17) shows that while entropy, like internal energy, cannot be destroyed, unlike internal energy, it can be *created* and, in fact, always *is* created in any spontaneously occurring process. Clausius (1850) stated this in the words: '*Die Entropie der Welt strebt einem Maximum zu' (The entropy of the universe tends towards a maximum).*

2.18 Dissipative Phenomena

Postulate IV is in accordance with the common experience that a real physical process is invariably accompanied by dissipative phenomena such as mechanical friction, turbulence, electrical resistance, viscosity, and others more. These dissipative phenomena (cf. § 7.3) manifest themselves as internally generated heat (cf. § 2.7), thus increasing the entropy of the system and decreasing the amount of energy available for work (cf. §§ 8.11, 8.14, and 8.17).

Production of entropy is the central problem of Part II of this text.

2.19 Infinitesimal Change in Heat

When only an adiabatic barrier is lifted in an isolated composite system, the infinitesimal change in internal energy in the subsystem under consideration equals the infinitesimal change in heat and is given by

$$dU = \delta Q = \left.\frac{\partial U}{\partial S}\right|_{X(\neq S)} dS\,. \tag{2.19}$$

2.20 Special Nature of Heat as a Form of Energy Exchange

Just like internal energy, entropy, the extensive parameter of heat, cannot be measured directly in the way in which the other extensive parameters, such as the volume and mole numbers, can be measured. This, together with the fact that entropy is not a conserved quantity in an isolated system, imparts a special status to heat as a form of energy exchange. This, indeed, is the reason for the existence of thermodynamics as a special branch of mechanics.

2.21 Limit of Entropy – POSTULATE V — The Third Law of Thermodynamics

According to Postulate V:

> *"The entropy of any finite system is positive semi-definite in the state for which the partial derivative of the internal energy with respect to the entropy vanishes".*

The state just referred to is characterized by the relation

$$\left.\frac{\partial U}{\partial S}\right|_{X(\neq S)} = 0\,. \tag{2.21}$$

Postulate V embodies one form of the *Third Law of Thermodynamics* (see § 7.19 for other formulations of the Third Law).

2.22 Monotonic Property of the Entropy

It follows from Postulate V that

$$\left.\frac{\partial S}{\partial U}\right|_{X(\neq U)} \geq 0\,, \tag{2.22}$$

i.e., the entropy is a monotone non-decreasing function of the internal energy.

2.23 Significance of the Concept of Entropy

The recognition that energy can always be factored into the product of an extensive and an intensive parameter lead to our introduction of the entropy as the extensive parameter of heat. The identification of the entropy as an extensive parameter of any thermodynamic system makes it possible to extend the theory of mechanical equilibrium to thermodynamic equilibrium involving thermal effects.

3. THE FUNDAMENTAL EQUATION

A functional relation between *all extensive* parameters of a thermodynamic system is called its *fundamental equation* (Gibbs, 1948). The fundamental equation contains all of the thermodynamic information on the system. Thermodynamic theory does not depend on the knowledge or even the existence of an *explicit form* of the fundamental equation. If one can, indeed, be formulated, it is bound to be rather complicated in general, because the constitution of the matter of which the thermodynamic system is composed will necessarily be complex. Thus, precious few explicit fundamental equations have been proposed and these all describe particularly simple systems (cf. §§ 12.1, 15.1, and 17.13). It is, nevertheless, crucial to an understanding of thermodynamic theory to examine the formal aspects and properties which characterize *any* fundamental equation, whether its explicit form is known or not. This is the task of the present chapter.

3.0 Chapter Contents

3.1 The Entropy and Internal Energy Representations of the Fundamental Equation

The functional relation

$$f(U, S, \dots, X_k, \dots) = 0 \tag{3.1$_1$}$$

is a first-order homogeneous equation of the extensive parameters of the system. Since U and S are the only two extensive parameters that cannot be measured directly (cf. §§ 2.8 and 2.20), we cast Eq.(3.1)$_1$ in either of two equivalent forms, explicit either for the internal energy, U, or the entropy, S. In the latter case we have

$$S = S(U, \dots, X_k, \dots)\,, \tag{3.1$_2$}$$

and speak of the *entropy function*, or the fundamental equation in the *entropy representation*. The extensive variables of state $U, \dots, X_k, \dots$, are called the 'natural' or 'canonical' variables in the entropy representation.

Since, by Postulates III and V, the entropy, S, is a continuous, differentiable, monotone non-decreasing function of U, Eq.(3.1)$_2$ can be inverted to give

$$U = U(S, \dots, X_k, \dots). \tag{3.1$_3$}$$

Equation (3.1)$_3$ is called the *energy function*, or the fundamental equation in the internal energy representation, or simply the *energy representation*. The extensive variables of state $S, \dots, X_k, \dots$, are called the 'natural' or 'canonical' variables in the energy representation.

The entropy and the energy representations are two different but equivalent ways of representing the same fundamental equation. Other representations will be introduced in Chapter 8. However, the entropy and the energy representations are the only ones whose canonical variables consist exclusively of extensive parameters. The energy function, U, and the entropy function, S, may be called the *cardinal functions* of equilibrium thermodynamics.

3.2 The Fundamental Surface in Thermodynamic Configuration Space

The fundamental equation defines a surface, the *fundamental surface*, in *thermodynamic configuration space* (Gibbs space). The coordinates of this space are the extensive parameters S, U, and X_k. For the *physical simple system* these parameters become simply S, U, and V. Hence, the fundamental equation of this system can be represented by a surface in three-dimensional Euclidean space as shown schematically in Fig. 3.2.

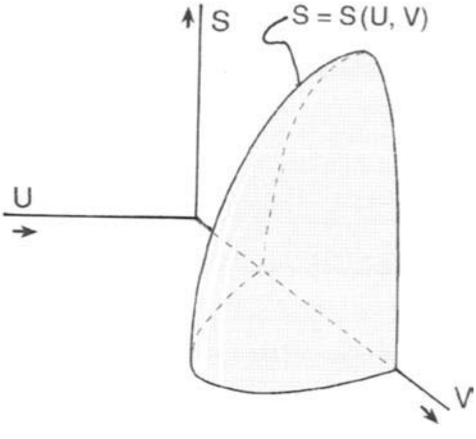

Fig. 3.2 The surface $S = S(U, V)$ in S, U, V – space

3.3 The Intensive Parameters in the Energy Representation

The differential form of the fundamental equation in the energy representation becomes

$$dU = \left.\frac{\partial U}{\partial S}\right|_{X(\neq S)} dS + \sum\nolimits_k \left.\frac{\partial U}{\partial X_k}\right|_{X(\neq X_k)} dX_k \qquad (3.3)_1$$

where $k = 1, 2, \ldots, r, \ldots$. We recognize the first term on the right as the right hand side of Eq.(2.19), and the second term as containing the right hand sides of both Eqs.(2.11) and (2.12).

In accordance with the factorability of the energy, the first-order partial derivatives in Eq.$(3.3)_1$ are recognized as the *intensive parameters* of the system in the *energy representation*. We denote the general intensity parameter in this representation by Y, and write

$$dU = Y_0\, dS + \sum\nolimits_k Y_k\, dX_k, \qquad (3.3)_2$$

where

$$Y_0 = \left.\frac{\partial U}{\partial S}\right|_{X(\neq S)} \qquad (3.3)_3$$

and

$$Y_k = \left.\frac{\partial U}{\partial X_k}\right|_{X(\neq X_k)}. \qquad (3.3)_4$$

The nature of the Y_k depends on the system considered. When $k = 1, 2, \ldots, r$, we shall let the $Y_k dX_k$ represent *physical work terms*. When $k = r + 1, \ldots$, the $Y_k dX_k$ will represent chemical work, i.e., *mass action terms*.

3.4 The Intensive Parameters in the Entropy Representation

In the entropy representation the differential form of the fundamental equation becomes

$$dS = \left.\frac{\partial S}{\partial U}\right|_{X(\neq U)} dU + \sum\nolimits_k \left.\frac{\partial S}{\partial X_k}\right|_{X(\neq X_k)} dX_k\,. \qquad (3.4)_1$$

where the first-order partial derivatives are the *intensive parameters* of the system in the *entropy representation*. We denote them by I, and write

$$dS = I_0\, dU + \sum\nolimits_k I_k\, dX_k \qquad (3.4)_2$$

where

$$I_0 = \left.\frac{\partial S}{\partial U}\right|_{X(\neq U)} \tag{3.4$_3$}$$

and

$$I_k = \left.\frac{\partial S}{\partial X_k}\right|_{X(\neq X_k)} \tag{3.4$_4$}$$

Again, when $k = 1, 2, \ldots, r$, the $I_k dX_k$ represent *physical work terms*, and when $k = r + 1, \ldots$, they represent chemical work, i.e., *mass action terms*.

3.5 The Intensity Factor of Heat – The Thermodynamic Temperature

Postulate III established entropy as the capacity factor of heat. In accordance with the factorability of the energy we identify Y_0 in Eq.(3.3)$_2$ with the *thermodynamic temperature*, T, the intensity factor of heat. The differential form of the fundamental equation in the energy representation thus becomes

$$dU = TdS + \sum_k Y_k \, dX_k \tag{3.5$_1$}$$

where TdS is the *heat term* and the remainder are the *work terms*. The partial derivatives in Eqs.(2.19) and (2.21) are now also recognized to represent the temperature, T.

We note that by Postulate V, i.e. by the monotonic property of the entropy (§ 2.22), the thermodynamic temperature is positive semi-definite.

In an analogous manner the partial derivatives in Eqs.(2.22) and (3.4)$_3$ are seen to be the *reciprocal thermodynamic temperature*, $1/T$. Thus,

$$I_0 = \frac{1}{T} \qquad \text{and} \qquad I_k = -\frac{Y_k}{T}, \tag{3.5$_2$}$$

and the differential form of the fundamental equation in the entropy representation thus becomes

$$dS = \frac{1}{T}\, dU - \sum_k I_k \, dX_k \tag{3.5$_3$}$$

where dU/T is the *heat term* while the remaining terms are the work terms.

In both representations of the fundamental equation we distinguish the heat terms from the work terms because of the special nature of heat as a form of energy exchange (§ 2.20).

3.6 Conjugate Parameters

The pairs of intensive and extensive parameters T and S, and Y_k and X_k in the energy representation, as well as $1/T$ and U, and I_k and X_k in the entropy representation, are *conjugate parameters*. The product of conjugate parameters in the energy representation have the dimensions of energy while that of conjugate parameters in the entropy representation have the dimensions of entropy.

The lowest value of subscript k will always be 1. We shall use subscript j instead of k when the lowest value is 0, and m when the lowest value is 2.

3.7 The Chemical Potential

We call the intensive parameters furnished by the first-order partial derivatives of the internal energy, when taken with respect to the mole numbers,

$$\left.\frac{\partial U}{\partial N_k}\right|_{X(\neq N_k)} = \mu_k\,, \qquad (k = r+1, \ldots) \qquad (3.7)$$

the *chemical potentials*. The concept of the chemical potential is again due to Gibbs (1948). The name reflects the fact that the internal energy, U, may be considered a potential for chemical work (cf. § 8.4). Thus, we recognize the $\mu_k dN_k$ $(k = r+1, \ldots)$ terms in Eq.(3.3)$_3$ as the mass action terms or *chemical work* terms. Just as in the case of the entropy (cf. § 2.13) the chemical potential, μ, is required by the factorability of the energy as the intensity factor in the product μN, the mole number, N, supplying the extensive factor (cf. § 1.5).

Unlike the other intensive parameters, the chemical potential cannot be measured directly. Its relation to measurable physical quantities is in the form of a differential equation [see Eq.(8.22)$_5$)]. Since the solution of such an equation requires a constant of integration, absolute values of the chemical potential must be defined relative to a judiciously chosen reference state (cf. § 12.12). Generally, however, only the *change* in chemical potential is of interest.

3.8 Significance of the Chemical Potential

The chemical potential is required by the factorability of the energy (cf. § 1.5) as the intensity parameter of mass action. It is the driving force for any change in the chemical composition of matter as specified by the mole numbers. The introduction of the concept of the chemical potential thus extends the scope of thermodynamics to the treatment of *open systems*, i.e., to systems which exchange matter with their surroundings, of *phase transitions*, i.e., transitions between homogeneous subsystems bounded by a surface across which the physical properties change discontinuously (see Chapter 19), and of *reactive systems*, i.e., to systems in which changes in composition occur as a result of chemical reactions (see Chapter 20).

3.9 The Gibbs Equation

The differential forms of the fundamental equation, Eqs.(3.5)$_1$ and (3.5)$_3$, are commonly called the *Gibbs equations*. For the *(multicomponent) simple system* these equations become

$$dU = TdS - PdV + \sum\nolimits_m \mu_m dN_m \tag{3.9$_1$}$$

in the energy representation, and

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \sum\nolimits_m \frac{\mu_m}{T} dN_m \tag{3.9$_2$}$$

in the entropy representation. In writing these equations we have taken into account that—for the simple system—pressure-volume work is the only physical work admitted. Thus, X_1 is the volume, V, and $-Y_1$ is the pressure, P, of the simple system.

For a single component simple system the above equations become simply

$$dU = TdS - PdV + \mu dN \tag{3.9$_3$}$$

and

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN\,. \tag{3.9$_4$}$$

in the energy and entropy representations, respectively.

3.10 The Euler Equation

Since the internal energy is a first-order homogeneous equation of the extensive variables of the system (Postulate I), we may write

$$U(\lambda S, \ldots, \lambda X_k, \ldots) = \lambda U(S, \ldots, X_k, \ldots) \tag{3.10$_1$}$$

where λ is a scaling parameter. Differentiating with respect to λ and then letting $\lambda = 1$ we obtain the energy function in the form

$$U = \sum\nolimits_j Y_j X_j \tag{3.10$_2$}$$

where the Y_j are given by Eqs.(3.3)$_3$ and (3.3)$_4$. Equation (3.10)$_2$ is called the *Euler equation in the energy representation.* It equates the energy function to the (algebraic) sum of the products formed from the conjugate parameters of the system.

The entropy function takes the form

$$S = \sum\nolimits_j I_j X_j\,. \tag{3.10$_3$}$$

where the I_j are defined by Eqs.(3.4)$_3$ and (3.4)$_4$. Equation (3.10)$_3$ is called the Euler equation in the entropy representation. It equates the entropy function to the (algebraic) sum of the products formed from the conjugate parameters of the system.

For the *(multicomponent) simple system* the cardinal functions become

$$U = TS - PV + \sum\nolimits_m \mu_m N_m \tag*{(3.10)$_4$}$$

in the energy representation, and

$$S = \frac{1}{T}U + \frac{P}{T}V - \sum\nolimits_m \frac{\mu_m}{T}N_m \tag*{(3.10)$_5$}$$

in the entropy representation.

The cardinal functions are connected through the relation

$$U = -TS\,. \tag*{(3.10)$_6$}$$

Indeed, multiplication of Eq.(3.10)$_5$ by $-T$ and rearranging leads at once to Eq.(3.10)$_4$.

3.11 Equations of State

A functional relation expressing an intensive parameter in terms of the extensive parameters of the system is called an *equation of state*. An equation of state is a zeroth-order homogeneous equation of the extensive parameters of the system.

The equations of state are obtained as the partial derivatives of the Euler equation. In the energy representation they are, therefore,

$$Y_j = Y_j(S, \ldots, X_k, \ldots) = \left.\frac{\partial U}{\partial X_j}\right|_{X_{i\neq j}} \tag*{(3.11)$_1$}$$

and the entropy representation they become

$$I_j = I_j(U, \ldots, X_k, \ldots) = \left.\frac{\partial S}{\partial X_j}\right|_{X_{i\neq j}}\,. \tag*{(3.11)$_2$}$$

For the *(multicomponent) simple system* we have

$$Y_0 = \left.\frac{\partial U}{\partial S}\right|_{X_{j\neq 0}} = T \tag*{(3.11)$_{3.1}$}$$

$$Y_1 = \left.\frac{\partial U}{\partial V}\right|_{X_{j\neq 1}} = P \tag{3.11$_{3.2}$}$$

and

$$Y_2 = \left.\frac{\partial U}{\partial N_m}\right|_{X_{j\neq 2}} = \mu_m \tag{3.11$_{3.3}$}$$

in the energy representation, and

$$I_0 = \left.\frac{\partial S}{\partial U}\right|_{X_{j\neq 0}} = \frac{1}{T} \tag{3.11$_{4.1}$}$$

$$I_1 = \left.\frac{\partial S}{\partial V}\right|_{X_{j\neq 1}} = \frac{P}{T} \tag{3.11$_{4.2}$}$$

and

$$I_2 = \left.\frac{\partial S}{\partial N_m}\right|_{X_{j\neq 2}} = \frac{\mu_m}{T} \tag{3.11$_{4.3}$}$$

in the entropy representation.

3.12 Relation between the Fundamental Equation and the Equations of State

Equations of state are generally much easier to establish than fundamental equations. However, in contrast to a fundamental equation, an equation of state does not contain complete information on the thermodynamic system. This follows from the fact that the intensive variables are (partial) *derivatives* of the extensive ones. The differentiation results in a loss of information. Nevertheless, the *totality* (i.e., *the complete set*) of the equations of state is equivalent to the fundamental equation. To recover the latter it is only necessary to insert all the state equations into the Euler equation from which were derived (cf. §§ 12.3 and 13.8). Since we thus regain the *complete* information on the system, this is tantamount to an integration. The Euler equation in either representation is therefore a form of the fundamental equation.

4. THERMODYNAMIC EQUILIBRIUM

Chapters 2 and 3 developed the basic armamentarium of the theory of equilibrium thermodynamics. We are now ready to address its central problem: *the conditions of thermodynamic equilibrium* (§ 1.11). In particular, we consider the conditions under which an isolated composite system returns to a state of equilibrium after the lifting of an internal constraint (the removal of a barrier).

4.0 Chapter Contents

4.1 Representation of Equilibrium in Gibbs Space

An equilibrium state (§ 1.12) is represented by a point in thermodynamic configuration space. The equilibrium states accessible to a given system lie on the fundamental surface.

4.2 Extremum Principles

An extremum principle minimizes or maximizes the fundamental equation subject to certain constraints. The principle of maximum entropy and its equivalent, the principle of minimum internal energy, are the fundamental principles of equilibrium thermodynamics. Alternative extremum principles will be introduced in Chapter 8.

4.3 The Maximum Principle for the Entropy

In accordance with Postulate IV, upon the removal of an internal barrier in an isolated composite system the extensive parameters of the system assume those values which maximize the entropy over the manifold of equilibrium states consistent with the remaining constraints. The extremum principle for the entropy states:

> *"At equilibrium the value of any unconstrained parameter of an isolated thermodynamic system is such that the entropy is maximized at constant internal energy".*

The *entropy maximum principle* thus characterizes the equilibrium state as one of maximum entropy for a given total internal energy. Figure 4.3 illustrates this for the *physical simple system*

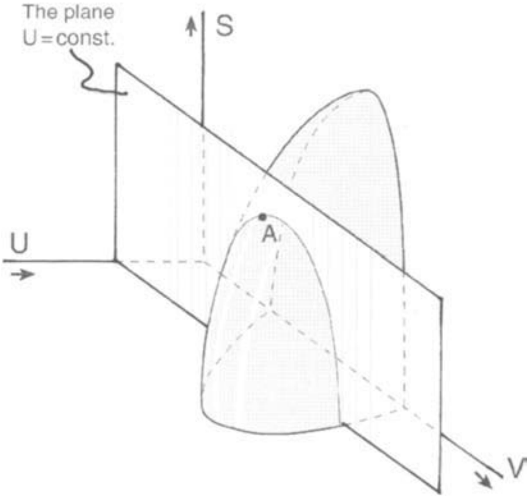

Fig. 4.3 The equilibrium state **A** as a point of maximum S for constant U

Mathematically the principle is expressed by the usual conditions for a maximum, i.e., by

$$(dS)_U = 0 \qquad \text{and} \qquad (d^2S)_U < 0\,. \tag{4.3}$$

The first of these is the *condition* (or *criterion*) *of thermodynamic equilibrium*. The second is the *condition* (or *criterion*) *of thermodynamic stability* which will form the subject of Chapter 18.

4.4 The Extremum Principle for the Internal Energy

An equivalent extremum principle can also be established for the internal energy as illustrated below in Figure 4.4, again for the *physical simple system*.

The *energy minimum principle* characterizes the equilibrium state as one of minimum energy for a given total entropy. It reads:

> *"At equilibrium the value of any unconstrained parameter of an isolated thermodynamic system is such that the internal energy is minimized at constant entropy".*

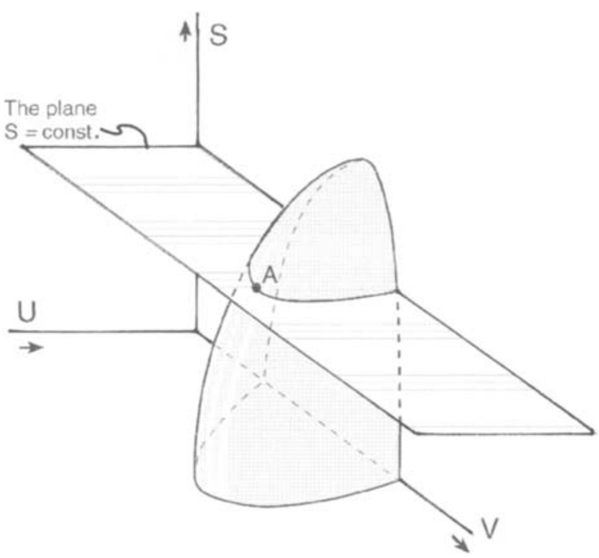

Fig. 4.4 The equilibrium state A as a point of minimum U for constant S

Mathematically this is expressed by the conditions for a minimum, i.e., by

$$(dU)_S = 0 \qquad \text{and} \qquad (d^2U)_S > 0 \tag{4.4}$$

where the first is again the *condition* (or *criterion*) *of thermodynamic equilibrium*, and the second is the *condition* (or *criterion*) *of thermodynamic stability* (see Chapter 18).

4.5 Equivalence of the Extremum Principles for the Energy and the Entropy

The extremum principles for the internal energy and for the entropy express the condition of equilibrium of the isolated thermodynamic system in the entropy representation and in the energy representation, respectively. They are thus equivalent and may be used interchangeably.

To prove this assertion, assume that, upon the establishment of a new equilibrium, the internal energy is not minimum while the entropy is maximum. It would then be possible to withdraw work from the system at constant entropy, and reinject it in the form of heat. This would restore the system to its original energy. However, the resultant increase in entropy would be inconsistent with the requirement that the equilibrium state be one of maximum entropy. Consequently, the two extremum principles imply each other.

4.6 Equilibrium Conditions in Terms of the Intensive Parameters: The Diathermal Case – Energy Representation

The conditions of thermodynamic equilibrium were stated in §§ 4.3 and 4.4 in terms of the extensive parameters, U and S. Equilibrium conditions can, however, also be established in terms of the intensive parameters. Here, and in §§ 4.7 to 4.9 we discuss these conditions as they apply to a *single-component simple system.* Generalization to *multicomponent simple systems* and to *non-simple systems* is straight-forward.

We distinguish two cases: the diathermal and the adiabatic case. We first investigate the conditions of equilibrium in the diathermal case in the energy representation.

Removal of a barrier, inside an isolated *composite system*, each a *single-component simple system*, both composed of the same kind of matter, lifts the constraints of adiabaticity, rigidity, and impermeability between the two subsystems.

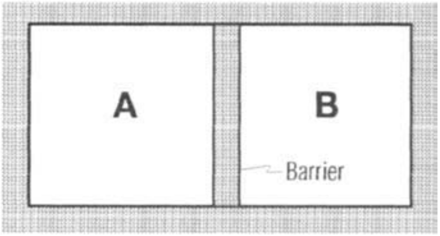

Fig. 4.6 Isolated composite system consisting of two subsystems, **A** and **B**

Since the *composite system* as a whole is isolated, the following *conservation (isolation) constraints* apply:

$$S_A + S_B = \text{constant} \qquad dS_A = -\,dS_B \qquad (4.6)_{1.1}$$

$$V_A + V_B = \text{constant} \qquad dV_A = -\,dV_B \qquad (4.6)_{1.2}$$

$$N_A + N_B = \text{constant} \qquad dN_A = -\,dN_B \qquad (4.6)_{1.3}$$

Equations $(4.6)_1$ state that the total entropy, volume, and number of moles of the *composite system* remain constant in a virtual change of the internal energy at equilibrium. The internal energy being additive, it follows by Eq.$(3.10)_1$ and the condition of equilibrium, $dU = 0$, that

$$dU = (T_A - T_B)\,dS_A - (P_A - P_B)\,dV_A + (\mu_A - \mu_B)\,dN_A = 0 \qquad (4.6)_2$$

Because dSA, dVA, and dNA represent infinitesimal changes in independent variables, we must have

$$T_\mathrm{A} = T_\mathrm{B} \tag{4.6)$_{3.1}$ }$$

$$T_\mathrm{A} = T_\mathrm{B} \qquad (4.6)_{3.1}$$

$$P_\mathrm{A} = P_\mathrm{B} \qquad (4.6)_{3.2}$$

and

$$\mu_\mathrm{A} = \mu_\mathrm{B} \qquad (4.6)_{3.3}$$

when equilibrium is reestablished after removal of the barrier. Equations $(4.6)_3$ are the equilibrium conditions in terms of the intensive variables in the energy representation. They express, respectively, the criteria of *thermal, mechanical,* and *diffusional* equilibrium. The corresponding stability criteria will be discussed in § 18.8 to 18.11.

4.7 Equilibrium Conditions in Terms of the Intensive Parameters: The Diathermal Case – Entropy Representation

We now examine the conditions of equilibrium in the diathermal case in the entropy representation. The first of the conservation constraints becomes

$$U_\mathrm{A} + U_\mathrm{B} = \text{constant} \qquad dU_\mathrm{A} = -dU_\mathrm{B} \qquad (4.7)_1$$

and the other two remain unchanged. Thus now the total energy, volume, and number of moles of the composite system are constant in a virtual change of the entropy at equilibrium. It follows by the condition of equilibrium, $dS = 0$, that

$$dS = \left(\frac{1}{T_\mathrm{A}} - \frac{1}{T_\mathrm{B}}\right) dU_\mathrm{A} + \left(\frac{P_\mathrm{A}}{T_\mathrm{A}} - \frac{P_\mathrm{B}}{T_\mathrm{B}}\right) dV_\mathrm{A} - \left(\frac{\mu_\mathrm{A}}{T_\mathrm{A}} - \frac{\mu_\mathrm{B}}{T_\mathrm{B}}\right) dN_\mathrm{A} = 0 \qquad (4.7)_2$$

and this furnishes the equilibrium conditions

$$\frac{1}{T_\mathrm{A}} = \frac{1}{T_\mathrm{B}} \qquad (4.7)_{3.1}$$

$$\frac{P_\mathrm{A}}{T_\mathrm{A}} = \frac{P_\mathrm{B}}{T_\mathrm{B}} \qquad (4.7)_{3.2}$$

$$\frac{\mu_\mathrm{A}}{T_\mathrm{A}} = \frac{\mu_\mathrm{B}}{T_\mathrm{B}} \qquad (4.7)_{3.3}$$

in the entropy representation. Equations $(4.6)_3$ and $(4.7)_3$ are clearly equivalent.

4.8 Equilibrium Conditions in Terms of the Intensive Parameters: The Diathermal Case – Partial Barrier Removal

If the barrier remains rigid and only the constraints of adiabaticity and impermeability are lifted, $dV_A = dV_B = 0$, and only the first and third of the equilibrium conditions are obtained in either the energy or the entropy representation. Similarly, when the barrier remains impermeable so that only the constraints of adiabaticity and rigidity are lifted, $dN_A = dN_B = 0$, and only the first and second of the equilibrium conditions ensue. Finally, when the barrier remains rigid and impermeable and only the constraint of adiabaticity is lifted, only the first of the equilibrium conditions results.

In all four cases in which the barrier becomes diathermal, the equilibrium conditions are sufficient to characterize the equilibrium state. Although we may have no equilibrium condition in terms of the pressures or chemical potentials, the system remains fully determined because the corresponding extensive parameters, the volumes or mole numbers, are known since they can be measured before the barrier is lifted and they remain constant thereafter.

4.9 Equilibrium Conditions in Terms of the Intensive Parameters: The Adiabatic Case

The special nature of heat as a form of energy exchange (§ 2.20) renders the adiabatic case indeterminate. Let us again remove a barrier between two subsystems of an isolated *composite system*, each a *single-component simple system*, and both composed of the same kind of matter. If the barrier remains adiabatic but becomes movable and permeable, there is no heat flux and the energy transfer between the two subsystems consists only of work and/or mass action. Hence, by the energy minimum principle,

$$dU = -(P_A - P_B)\, dV_A + (\mu_A - \mu_B)\, dN_A = 0\,. \tag{4.9}$$

Thus we recover the second and third of the equilibrium conditions we had found for the diathermal case, but no condition can be found for the temperatures. Clearly, if the barrier is adiabatic and impermeable, we obtain only $P_A = P_B$, while, if it is adiabatic and rigid, we can find only $\mu_A = \mu_B$.

Application of the entropy maximum principle furnishes the same indeterminate result. Therefore, if the barrier remains adiabatic, nothing can be said about the temperatures in the two subsystems and their entropies are not known because they cannot be measured directly. Indeed, it would be possible to withdraw a certain amount of heat from one subsystem and inject another amount into the other so that $dS_A = -dS_B$. The system could again be brought to equilibrium but the entropies of the subsystems would have changed. Thus, in the adiabatic case, the system is not completely determined.

4.10 Direction of Change in the Attainment of Equilibrium

Lifting only the adiabatic constraint, Eq.$(4.7)_2$ may be rewritten as

$$\Delta S \simeq \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\Delta U_A \tag*{$(4.10)_1$}$$

where we have assumed, for the sake of simplicity, that $T_A \simeq T_B$, and that the changes are finite. If $T_A > T_B$, then, since ΔS is necessarily positive, $\Delta U_A < 0$, i.e., the internal energy in subsystem A decreased, hence heat flowed from subsystem A to subsystem B. Thus:

> *"Heat flows from the hotter to the colder body",*

in accordance with common experience.

Removing only the constraint of rigidity and letting $T_A = T_B = T$, Eq.(4.7)$_2$ becomes

$$dS = \frac{P_A - P_B}{T}\, dV_A\,. \tag{4.10$_2$}$$

If $P_A < P_B$, then dV_A is necessarily negative, i.e., the volume of subsystem A has decreased, i.e.,

> *"An increase in pressure decreases the volume".*

This again is in accordance with normal expectation.

Finally, let us assume that the impermeable wall has been made permeable but stays rigid while the temperatures are the same. We then have

$$dS = \frac{\mu_A - \mu_B}{T}\, dN_A\,. \tag{4.10$_3$}$$

If $\mu_A > \mu_B$, then dN_A must be negative. This leads to the conclusion that:

> *"Matter flows from regions of high to regions of low chemical potential."*

The statement may be interpreted as saying that matter flows from regions of high concentrations to those of lower ones, once again in accordance with normal experience.

4.11 Multibody Thermal Equilibrium — The Zeroth Law of Thermodynamics

Repeated application of the procedure outlined in § 4.6, removing adiabatic barriers only, leads to the following realization:

> *"Two bodies that are in thermal equilibrium with a third body will be in thermal equilibrium with each other".*

This statement, known as the Zeroth Law of Thermodynamics, is the basis of *thermometry*.

5. THERMODYNAMIC PROCESSES

The lifting of a constraint in a *composite system* in an equilibrium state that is compatible with the constraint leads to a new state of equilibrium (§ 1.11). The transition from state A to state B is called a *process* (§ 1.13). This chapter looks at these thermodynamic processes.

5.0 Chapter Contents

5.1 Quasistatic Processes

Any real physical process is a temporal evolution of both equilibrium and non-equilibrium states and, as such, proceeds at a finite rate. In the limit that the process evolves infinitely slowly, it becomes an infinitely dense succession of equilibrium states, i.e., it becomes quasistatic (cf. § 1.13). A quasistatic process is represented by a 'locus' (i.e., a succession of points) on the surface in thermodynamic configuration space defined by the fundamental equation. Figure 5.1 below shows such a succession of points.

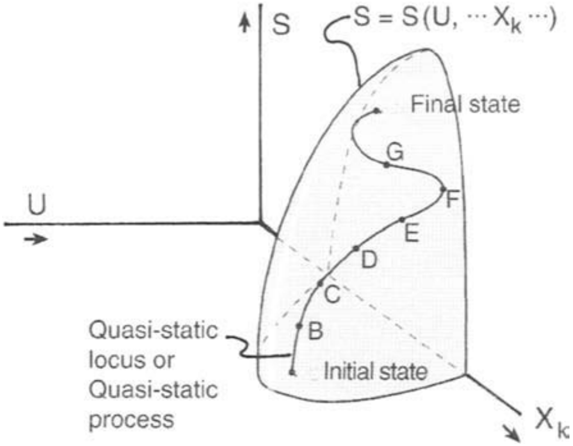

Fig. 5.1 Representation of a quasistatic process in thermodynamic configuration space

For simplicity the surface $S = S(U, \ldots, X_k, \ldots\ )$ is displayed as a function, in addition to the internal energy, of only one out of the totality of the extensive parameters, X_k, of a *composite system*.

5.2 Reversible Processes

If, in a thermodynamic process, the system *and* its surroundings are at equilibrium with each other at all times, a reversal of the direction of the process does not require any external agency. Such a process is called reversible. There is no internally generated heat. At the conclusion of a reversible process the state of the system is the same as it was before the process began (cf. §1.13) and the change in total entropy is zero, i.e.,

$$dS_{\text{Total}} = 0\ . \tag{5.2}$$

The process thus proceeds at constant total entropy as illustrated in Fig. 5.3. Such a 'isentropic' reversible process would proceed from state **A** to state **B** along the intersection of the $S = const$ plane with the fundamental surface (§ 3.2). The coordinates of the surface in the thermodynamic configuration space span the *composite system* consisting of the system of interest as one, and its surroundings as another, subsystem. A reversible process is necessarily quasistatic although the converse is not true. Figure 5.1 illustrates a quasistatic process which is not isentropic and, hence, not reversible.

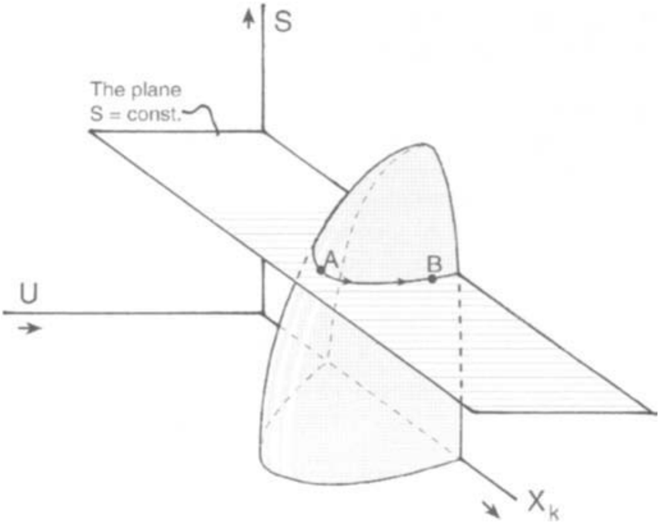

Fig. 5.3 A reversible process proceeding along a quasistatic isentropic locus

A reversible, i.e., isentropic quasistatic process is essentially a useful artifice representing an ideal limiting case. Many real physical processes do, however, approach reversibility surprisingly closely. This is especially true of mechanical processes in which friction effects can often be kept to a bare minimum.

5.3 The Clausius Equality

Comparison of Eqs.$(2.6)_2$ and $(3.5)_1$ reveals the quasistatic heat flux, δQ, to be equal to the heat term, TdS, and it follows that the infinitesimal change in entropy thus becomes

$$dS = \delta Q/T\,. \tag{5.3}$$

Equation (5.3) is called the *Clausius equality.*

5.4 Measurability of Entropy Changes

The Clausius equality enables us to measure changes in entropy in a quasistatic (reversible) process. The reciprocal temperature, $1/T$, is recognized as an *integrating factor* which permits integration of the inexact differential, δQ. The integration yields the finite change in entropy as

$$\Delta S = \int \frac{\delta Q}{T} = \frac{Q}{T}\,, \tag{5.4}$$

and, since Q can be measured (cf. § 2.9), the change in entropy can be obtained by dividing the quasistatic heat flux, Q, by the temperature, T.

5.5 The Clausius Inequality — The Second Law of Thermodynamics

By Postulate IV a real physical process (a spontaneous natural process) is always accompanied by an increase in entropy (cf. § 2.17). Therefore, the change in entropy taking place in a real physical process is always greater than the change which would occur as the result of a quasistatic heat flux. This is expressed by the *Clausius Inequality*

$$dS \geq \delta Q/T \tag*{$(5.5)_1$}$$

in which the equal sign applies only to the limiting case of a quasistatic process. The inequality is commonly referred to as a mathematical expression of the *Second Law of Thermodynamics* (cf. § 7.17).

Making use of the internally generated heat (cf. § 2.7), we can rewrite Eq.$(5.5)_1$ as

$$dS = \delta Q/T + \delta Q'/T\,. \tag*{$(5.5)_2$}$$

The two Eqs. (5.5) become the Clausius equality when the internally generated heat vanishes.

5.6 Entropy Production

According to the foregoing, the elemental change in entropy can be divided into two parts. The first, d_eS, is the change in entropy arising from interactions with the exterior of the system. The second, d_iS, represents the entropy change produced in its interior due to internally generated heat. We therefore have

$$dS = \delta Q/T + \delta Q'/T = d_eS + d_iS\,. \tag{5.6)$_1$}$$

Postulate IV, formulated another way, states that

$$d_iS = \delta Q'/T \geq 0 \tag{5.6)$_2$}$$

i.e., the entropy created in the interior of a system is never negative. It vanishes only in a process in which there is no internally generated heat and, hence, no production of entropy in the interior of the system. Clearly, in that case $dS = d_eS$.

Equilibrium thermodynamics cannot say anything about the production of entropy in a real physical process. This, indeed, is the central problem of the thermodynamics of *non-equilibrium processes*. The quantitative determination of the entropy produced in a *steady-state process* will be the central problem of Part II.

5.7 Irreversible Processes

Any real physical process is *irreversible*. The very fact that the process is assumed to proceed implies that the entropy in the final state is greater than that in the initial state. It is impossible to reverse the process by manipulating constraints within the same isolated system because a manipulation resulting in a decrease in entropy in the isolated system would be a violation of the entropy maximum principle. The terms: real physical (or spontaneous natural) process and irreversible process, may be used interchangeably (cf. § 1.13).

5.8 Direction of an Irreversible Process

The direction of a real physical process is determined by the Clausius inequality. Such a process will proceed spontaneously only in the direction in which the total entropy of the isolated system in which the process occurs, increases (cf. § 4.10). A change in the opposing direction requires an external agency (cf. § 7.4).

For a real physical process to proceed spontaneously, the change in entropy at constant internal energy must increase and, concomitantly, the change in internal energy at constant entropy must decrease. In mathematical language this is expressed by

$$(dS)_U > 0 \qquad \text{and} \qquad (dU)_S < 0\,. \tag{5.8}$$

These relations therefore determine the direction of an irreversible process and should be compared with the equilibrium conditions given in §§ 4.3 and 4.4.

5.9 Irreversible Processes in Equilibrium Thermodynamics

The reason that at least some aspects of irreversible processes can be treated in equilibrium thermodynamics is the following: For every irreversible (i.e., real physical) process proceeding from an equilibrium state A to a new equilibrium state B, a reversible process may be devised which has the same initial equilibrium state A and final equilibrium state B. Thus, an ordered succession of equilibrium states may be substituted for the real physical process which is a temporal evolution of both equilibrium and non-equilibrium states. The state functions which characterize the equilibrium states are independent of the path through which the system has been taken and the end result is the same whether the path had been a highly idealized reversible path or an irreversible one.

6. REVERSIBLE SOURCES AND RESERVOIRS

We now introduce a set of idealized auxiliary thermodynamic systems with special properties that they possess by definition. These systems are the reversible work, heat, and matter sources[2] and reservoirs. We call them auxiliary systems because they serve as components in composite systems whose main component we wish to investigate. Their primary purpose is to assure constancy of one or the other intensive parameter (the temperature, pressure, or chemical potential) in the main component. Much use is made of these auxiliary systems in the next chapter but their use occurs frequently also elsewhere throughout this text.

6.0 Chapter Contents

6.1 Reversible Work Source (RWS)

A system enclosed by adiabatic impermeable walls in which all processes of interest are quasistatic is a *reversible work source*. When coupled to another system through a movable wall, a reversible work source acts as a quasistatic source or sink of work.

Since there is neither heat nor matter flux into or out of the reversible work source, it is at constant entropy, i.e. $dS^{\mathrm{RWS}} = 0$. There is an appropriate reversible work source for each kind of work. If the latter is pressure-volume work, the reversible work source is a reversible source of volume. In that case the change in internal energy becomes

$$dU^{\mathrm{RWS}} = \delta W^{\mathrm{RWS}} = -P^{\mathrm{RWS}}\, dV^{\mathrm{RWS}} . \qquad (6.1)$$

6.2 Work Reservoir (WR)

A very large reversible work source is called a *work reservoir*. In a work reservoir the intensive parameter of the work term is constant. If the work is pressure-volume work, the pressure of a volume reservoir (VR) is constant. Such a work reservoir acts as a *manostat*. It keeps the pressure of a coupled system constant at the value of its own pressure. The atmosphere can frequently be considered to be a good approximation to a volume reservoir.

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[2] The idealized system will be called a *source* regardless of whether it functions as a source or as a sink.

6.3 Reversible Heat Source (RHS)

A system enclosed by rigid impermeable walls in which all processes of interest are quasistatic is a *reversible heat source*. When coupled to another system through a diathermal wall, a reversible heat source acts as a quasistatic source or sink of heat.

Since the only energy exchange of the reversible heat source with any coupled system is a flux of heat, the change in internal energy within the reversible heat source is given by

$$dU^{\mathrm{RHS}} = \delta Q^{\mathrm{RHS}} = T^{\mathrm{RHS}}\, dS^{\mathrm{RHS}} . \tag{6.3}$$

6.4 Heat Reservoir (HR)

A very large reversible heat source is called a *heat reservoir*. The temperature of a heat reservoir is constant. A heat reservoir coupled to another system through a diathermal wall acts as a *thermostat*. It keeps the temperature of the coupled system constant at the value of its own temperature. The atmosphere can frequently be considered to be a good approximation to a heat reservoir.

6.5 Reversible Matter Source (RMS)

A system enclosed by rigid diathermal walls in which all processes of interest are quasistatic is called a *reversible matter source*. When coupled to another system through a permeable wall, a reversible matter source acts as a quasistatic source or sink of matter.

No work is exchanged with a reversible matter source. However, if the walls of the reversible matter source were adiabatic to exclude any flow of heat, its entropy would not be constant because of the flow of matter which carries its own entropy (cf. § 2.10). Hence, the walls of a reversible matter source must be diathermal as well as permeable and the reversible matter source is simultaneously a reversible heat as well as a reversible matter source.

There is an appropriate reversible matter source for each kind of matter. If several kinds are considered, the walls of the reversible matter source must be semi-permeable, i.e. permeable to one kind of matter only.

6.6 Matter Reservoir (MR)

A very large reversible matter source is called a *matter reservoir*. In a matter reservoir the chemical potential of the species of which it consists is constant. When coupled to another system through a semi-permeable wall, a matter reservoir keeps the chemical potential of the coupled system constant at the value of its own potential. It thus acts as a *chemostat*. The ocean can be considered to be a good approximation to a matter reservoir for sodium chloride.

6.7 Total Change in Entropy in Interaction with a Reversible Source

In the interaction of a given thermodynamic system with a reversible heat, work, or matter source the *total* change in entropy is zero because the processes are reversible.

7. WORK AND HEAT

This chapter inquires into the circumstances under which heat can be converted into work. The reverse, i.e., the conversion of work into heat, can always be accomplished completely, i.e., with 100% efficiency. Moreover, if the process is carried out isothermally—removing the heat generated or supplying the heat needed—the system that accomplishes the conversion remains itself unchanged at the end of the process. The process can therefore be continued indefinitely. The situation is quite different when heat is converted into work. This is another manifestation of the special nature of heat as a form of energy exchange (cf. § 2.20).

7.0 Chapter Contents

7.1 Conversion of Heat into Work

Although it is possible to convert heat into work completely, at the end of such a process the state of the system is changed. To illustrate: consider the isothermal expansion of an ideal gas. The system is attached to a heat reservoir (effectively a thermostat, cf. § 6.4) to ensure isothermal conditions. The internal energy of an ideal gas depends solely on the temperature (cf. § 12.2). Since this is constant, there is no change in internal energy. Hence, $\Delta U = W + Q = 0$, and the heat, Q, drawn from the heat reservoir is completely converted into the work of expansion, W. However, at the end of the process the volume as well as the pressure of the system are not what they were before the expansion. The state of the system thus has changed. To continue *ad libitum* a process of converting heat into work it is necessary to arrange a *cyclic process* in which the system is restored to its original state at the completion of each cycle. It turns out that this requires the sacrifice of a portion of the heat (cf. § 7.5 below). As a result, such a conversion never proceeds with 100% efficiency even if the conversion were carried out reversibly. It thus becomes necessary to establish the conditions under which the maximum amount of work can be extracted from a given process, and to consider how heat can be converted into work in a continuous cyclic operation.

7.2 Maximum Work and Maximum Mass Action Processes

Of all processes occurring between a given initial and a given final state of a system, the flux of heat is minimum, and the flux of work or matter is maximum, in the absence of internally generated heat, i.e., in a reversible process (cf. § 5.2). Thus, when a system is coupled to another system to which it delivers heat, work, or mass action, the heat delivered is minimum, and the work and the mass action are maximum, if the transfer is to a reversible heat, work, or matter source. We then speak of a maximum work process, or a maximum mass action process.

7.3 Useful Work and Lost Work

The maximum work that the system can deliver in a reversible process is *useful work*. In an irreversible, i.e., real physical process, this work is reduced by the portion lost to dissipative phenomena (cf. § 2.18) in the form of internally generated heat. This work is called *dissipative* or *lost work* although it is properly speaking a lost opportunity to extract work. Equilibrium thermodynamics does not inquire into the origin or the nature of the various dissipative effects (mechanical friction, viscosity, electrical resistance, etc.). It simply acknowledges their existence and provides a framework for dealing with them thermodynamically in an appropriate manner. It does that through the concept of entropy and, in particular, through that of the Clausius inequality (cf. § 5.5).

7.4 Decrease in Entropy in a Real Physical Process – Thermodynamic Engines

In an isolated thermodynamic system a real physical process is necessarily accompanied by an increase in entropy because an isolated system in equilibrium cannot spontaneously proceed to another equilibrium state with lower entropy (cf. § 5.8). However, in a cyclic process the system must be brought into a state of lower entropy as part of the cycle. This can be accomplished if the system is coupled with another, and if thereby the *total* entropy of the *composite* system increases. This principle can be illustrated with the help of idealized devices known as *thermodynamic engines*. They are either *heat engines*, or *heat pumps* and *refrigerators*. Coupled thermodynamic engines operate cyclically.

7.5 Principle of Operation of a Heat Engine

A heat engine is a device that converts heat into work. In the schematic below the heat engine withdraws an amount of heat, δQ^{h}, from a reversible heat source (the *hot* source) at the temperature T^{h}, rejects the amount of heat δQ^{c} to another reversible heat source (the *cold* source) at the temperature T^{c}, and delivers the difference, δW^{RWS}, to a reversible work source. The heat engine, the two reversible heat sources, and the reversible work source, form an isolated composite system in which the total change in internal energy is zero.

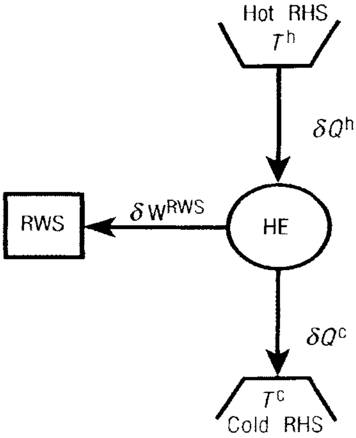

Fig. 7.5 Schematic of the operation of a heat engine

Hence, by the principle of the conservation of energy (§ 2.6),

$$dU = \delta W^{\mathrm{RWS}} + \delta Q^{\mathrm{h}} + \delta Q^{\mathrm{c}} = 0\,. \qquad (7.5)_1$$

Since the coupled processes considered are deemed to be reversible, the total change in entropy is also zero, i.e.,

$$d(S^{\mathrm{h}} + S^{\mathrm{c}}) = 0\,. \qquad (7.5)_2$$

The entropy in the *hot* source decreases. However, this decrease is exactly compensated by an equivalent increase of the entropy in the *cold* source. Since $T^{\mathrm{c}} < T^{\mathrm{h}}$, $\delta Q^{\mathrm{c}} = T^{\mathrm{c}} dS^{\mathrm{c}}$ is *less* than $\delta Q^{\mathrm{h}} = T^{\mathrm{h}} dS^{\mathrm{h}}$, the changes in entropy, dS^{c} and dS^{h}, being of the same magnitude. The difference in energy is available as work. From Eq.(7.5)$_1$ we obtain the work delivered to the reversible work source as

$$\delta W^{\mathrm{RWS}} = -\,\delta Q^{\mathrm{h}}\left[1 + \frac{\delta Q^{\mathrm{c}}}{\delta Q^{\mathrm{h}}}\right] = -\,\delta Q^{\mathrm{h}}\left[1 - \frac{T^{\mathrm{c}}}{T^{\mathrm{h}}}\right], \qquad (7.5)_3$$

the second of these equations following from Eq.(7.5)$_2$. The signs in Eq.(7.5)$_3$ are chosen from the viewpoint of the heat engine. The work, δW^{RWS}, is delivered *by* the heat engine, the heat, δQ^{h}, is delivered *to* it. The work is maximum because we have considered reversible processes. In an irreversible, i.e., real physical process, the work would not be maximum because of the occurrence of dissipative phenomena, but the principle of operation of the heat engine remains the same. Clearly, the total amount of the heat withdrawn, δQ^{h}, could be converted into work only if the heat could be rejected to a reservoir at $T^{\mathrm{c}} = 0$.

It is also clear that at the conclusion of the process the system is now at the temperature T^{c} whereas it originally was at T^{h}. Its thermodynamic state has therefore been changed. To operate cyclically it is necessary to reverse, as it were, the process just described so that at the end of the new process the system is returned to its original state (cf. § 7.10).

7.6 Efficiency of a Heat Engine

The fraction of the heat withdrawn that can be transformed into work is the *theoretical (thermodynamic) efficiency*, ϵ_{e}, of a heat engine. By Eq.(7.5)$_3$ it is given by

$$\epsilon_{\mathrm{e}} = \frac{-\delta W^{\mathrm{RWS}}}{\delta Q^{\mathrm{h}}} = \frac{T^{\mathrm{h}} - T^{\mathrm{c}}}{T^{\mathrm{h}}} \tag{7.6}$$

and is thus the ratio of $-\delta W^{\mathrm{RWS}}$, the work delivered to the reversible work source, to δQ^{h}, the heat extracted from the reversible heat source. If the process is irreversible, the efficiency of the heat engine is clearly less than the theoretical (thermodynamic) efficiency.

We note that ϵ_{e} is a *universal* function of two temperatures. It does not depend on the definition of the temperature scale on which the temperatures are measured.

7.7 Principle of Operation of Heat Pumps and Refrigerators

The thermodynamic heat engine just considered *delivers* work. In two other types of thermodynamic engine work is *absorbed*. A thermodynamic engine that converts work into heat is called either a *heat pump* or a *refrigerator* according to the way it is operated. A schematic of the operation of a heat pump is shown in Fig. 7.7 below.

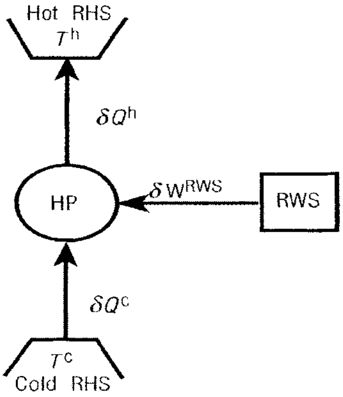

Fig. 7.7 Schematic of the operation of a heat pump

The engine absorbs the amount of work, δW^{RWS}, from a reversible work source, and the amount of heat, δQ^{c}, from a reversible heat source (the *cold* source) at the temperature T^{c}. It then delivers the amount of heat, δQ^{h}, to a reversible heat source (the *hot* source) at the temperature T^{h}. Since the hot source becomes hotter, the engine is a *heat pump.*

If the process is conducted in such a manner that the cold source becomes colder, the engine is called a *refrigerator.* In both cases the state of the system is altered from the original state at the end of the process.

7.8 Performance of a Heat Pump

The ratio of $-\delta Q^{\mathrm{h}}$, the heat delivered by the pump, to δW^{RWS}, the work absorbed by it is called the *coefficient of performance* of the heat pump. It is given by

$$\epsilon_{\mathrm{p}} = \frac{-\delta Q^{\mathrm{h}}}{\delta W^{\mathrm{RWS}}} = \frac{T^{\mathrm{h}}}{T^{\mathrm{h}} - T^{\mathrm{c}}} \; . \tag{7.8}$$

The work taken from the work source is minimized (i.e., the negative work is maximized) in a reversible process.

7.9 Performance of a Refrigerator

The *coefficient of performance* of a refrigerator is the ratio of δQ^{c}, the heat taken from the cold source, to δW^{RWS}, the work taken from the work source. It is given by

$$\epsilon_{\mathrm{r}} = \frac{\delta Q^{\mathrm{c}}}{\delta W^{\mathrm{RWS}}} = \frac{T^{\mathrm{c}}}{T^{\mathrm{h}} - T^{\mathrm{c}}} \; . \tag{7.9}$$

Again, the work required is minimized in a reversible process.

7.10 Cyclic Operation

To achieve the conversion of heat into work in a continuous cyclic process, the operation of a heat engine must be combined with that of a heat pump. Since the state of two thermodynamic engines operating in this manner is unchanged on completion of a full cycle, they effectively are not part of the process of converting heat into work. Such a combination is therefore often called an *auxiliary heat engine* when attention is focused on the conversion process as such.

7.11 The Carnot Cycle and the Carnot Engine

Many cyclic operations can be devised and many are of great practical importance. Historically the first to be described is the cycle named after its original investigator, Sadi Carnot (1878). We shall consider here only this, rather idealized, cycle because it is distinguished by its simplicity and by its fundamental importance. An engine operating under a *Carnot cycle*, i.e., a *Carnot engine*, is conceived to operate reversibly. This assures it of maximum efficiency. It is useful to know that *any* cyclic process can always be broken into an assembly of Carnot cycles[3] .

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[3] see, e.g., ter Haar and Wergeland (1966).

To consider the operation of a Carnot engine in detail we image an idealized system consisting of a cylinder filled with a suitable working fluid and provided with a frictionless movable piston. This *auxiliary engine* forms an isolated system with a reversible work source to which it is permanently attached, and with two heat reservoirs to either of which it can be attached or not, as needed. We consider heat reservoirs instead of reversible heat sources merely as a matter of convenience since it allows us to deal with finite instead of infinitesimal changes.

A full cycle of operation of the system will comprise four distinct steps. Since we are concerned with heat, we follow the changes in temperature (the intensive parameter of heat) and in entropy (the extensive parameter of heat) and plot them against one another on a T, S – diagram as

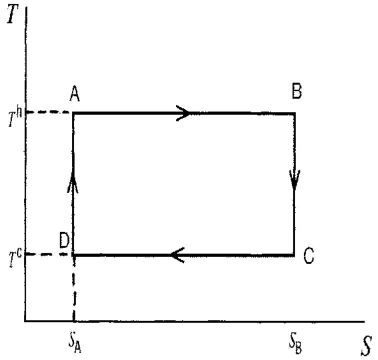

Fig. 7.11 T, S – diagram of a Carnot cycle

shown in Fig. 7.11. Other diagrams (e.g., a P, V – diagram) may, of course, be constructed and may be useful in various contexts.

Step 1. During the first two steps the system operates as a heat engine. At the beginning of the cycle we imagine it to be in contact with the hot, but not with the cold, heat reservoir. The working fluid is under pressure (the piston is latched) and is at the temperature, T^h, of the reservoir. Its state is represented by point A in the diagram. In the first step of the cycle we now allow the working fluid to undergo an isothermal expansion by freeing the latch. In this process the engine takes an amount of heat, $Q^h = T^h \Delta S$, from the heat reservoir and transfers a certain amount of work to the reversible work source. The process is isothermal (we move from point A to point B in the diagram along the upper isotherm AB).

Step 2. In the next step the engine is switched from the hot to the cold heat reservoir. The working fluid now expands adiabatically until its temperature reaches that of the cold reservoir, T^c. In this process a further amount of work is transferred to the reversible work source from the engine at the expense of the internal energy of the working fluid. There is no transfer of heat. Since the process is adiabatic and quasistatic, the change in entropy is zero, i.e., $\Delta S = 0$, and we move from point B in the diagram to point C along the right adiabat BC.

Step 3. At the end of the first two steps the thermodynamic state of the engine is altered. Its entropy and volume have increased, and its internal energy has decreased. To restore it to its original state, the first two steps are now reversed, in effect operating the engine as a heat pump. In the third step the working fluid is first attached to the cold heat reservoir and is then compressed isothermally. The reversible work source now performs work on the working fluid until its entropy attains its original value. We move from point C in the diagram to point D along the lower isotherm, CD. The engine transfers the amount of heat, $Q^{\mathrm{c}} = T^{\mathrm{c}}\Delta S$, to the cold heat reservoir.

Step 4. In the final step, the system is detached from the cold heat reservoir and the working fluid is further compressed adiabatically until its temperature reaches that of the hot heat reservoir, T^{h}, again. During this process the reversible work source performs more work There is no transfer of heat, and the change in entropy is zero, i.e., $\Delta S = 0$ as in Step 2. In the diagram we move from point D to point A along the left adiabat DA, thus completing the cycle. The internal energy and volume of the working fluid have now also been restored to their original values.

7.12 Analysis of the Carnot Cycle

The analysis of the complete cycle is simple. Because the engine has returned to its initial state at the end of the cycle, the total change in its internal energy is zero. Hence,

$$\Delta U = -W + Q^{\mathrm{h}} - Q^{\mathrm{c}} = 0\,, \qquad (7.12)_1$$

where W is the net work delivered to the reversible work source. W and Q^{c} are taken with the negative sign because they represent work and heat delivered *by* the engine. We have

$$W = Q^{\mathrm{h}} - Q^{\mathrm{c}} = (T^{\mathrm{h}} - T^{\mathrm{c}})\,\Delta S\,. \qquad (7.12)_2$$

There is a net transfer of work even though the engine works in reverse during part of the cycle. The net work delivered per cycle, W, is represented by the rectangular area ABCD in Fig. 7.11 while the areas AB$S_{\mathrm{B}}S_{\mathrm{A}}$ and DC$S_{\mathrm{B}}S_{\mathrm{A}}$ represent Q^{h} and Q^{c}, respectively.

Elimination of ΔS between $Q^{\mathrm{h}} = T^{\mathrm{h}}\Delta S$ and $Q^{\mathrm{c}} = T^{\mathrm{c}}\Delta S$ yields

$$\frac{Q^{\mathrm{h}}}{T^{\mathrm{h}}} = \frac{Q^{\mathrm{c}}}{T^{\mathrm{c}}}\,. \qquad (7.12)_3$$

The thermodynamic efficiency of the Carnot engine [cf. Eq.(7.6)] is given by

$$\epsilon_{\mathrm{C}} = \frac{W}{Q^{\mathrm{h}}} = 1 - \frac{T^{\mathrm{c}}}{T^{\mathrm{h}}}\,. \qquad (7.12)_4$$

The last two equations govern the cycle and are known as the *Carnot equations*.

7.13 The Complete Carnot Cycle

To recapitulate: In a complete Carnot cycle a quantity of heat is taken from a reversible heat source, part of it is rejected to another reversible heat source at a lower temperature, and the rest is delivered as work to a reversible work source. This is precisely the process we have outlined qualitatively in § 7.1. We have now carefully specified the steps in a cyclic operation which leaves the engine in its original state at the completion of the cycle.

Since the efficiency of the Carnot engine is maximal, any engine operating cyclically and reversibly between two temperatures follows the Carnot cycle and is a Carnot engine.

7.14 Thermodynamic Temperature Scale

Since W and Q are measurable (cf. § 2.9), the Carnot equations, Eqs.(7.12)$_3$ and (7.12)$_4$, allow us to obtain temperature ratios. When a suitable reference temperature has been selected, the temperature of any other body can, in principle, be determined independently of any material property of the thermometric substance or of the definition of the scale on which the temperatures are measured (cf. §§ 4.11 and 7.6). That real physical processes are never reversible, is a practical rather than a theoretical difficulty. Choosing the *triple point* of water (cf. § 19.14) as the reference temperature defines the *absolute thermodynamic temperature scale* or *Kelvin scale.*

7.15 The Dimensions of Entropy and of Temperature

By Eq.(3.10)$_4$ the product of entropy and temperature has the dimensions of energy. Within this restriction the *dimensions* of either factor can be selected arbitrarily. At least in thermodynamics, the entropy is best considered to be a dimensionless quantity. This is in accordance with the statistical mechanical view of entropy as a measure of randomness. The dimensions of temperature then become the dimensions of energy. Selection of suitable *units of measurement* for the entropy and/or the temperature is a matter of applied thermodynamics.

7.16 Poincaré Statement of the First Law

The First Law of thermodynamics (§ 2.6) can be recast as a general statement on the conversion of heat into mechanical work in a cyclic process. The statement, due to Poincaré, reads:

> *"In any cyclic process the work done by a system equals the heat received by it".*

Mathematically this can be expressed by the equation

$$\oint \delta W = \oint \delta Q \tag{7.16}$$

in which the integrals are circular integrals taken over a cycle, and W and Q are both expressed in the same units of measurement.

A device which would violate the First Law by allowing the extraction of more work from a system than the heat delivered to it, is called a *perpetuum mobile* (a perpetual motion device) *of the first kind.* The Poincaré statement asserts the impossibility of the existence of such a device.

7.17 Kelvin-Planck and Clausius Statements of the Second Law

The Second Law of thermodynamics (§ 5.5) can also be restated to apply specifically to cyclic processes. The Clausius statement has reference to heat pumps. It states:

> *"It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body".*

A device that *would* transfer heat from a cooler to a hotter body (in violation of the principle enunciated in § 4.10) would be a *perpetuum mobile of the second kind.* The Clausius statement thus asserts the impossibility of the existence of such a device.

The Kelvin-Planck statement has reference to heat engines. It states:

> *"It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work".*

The Kelvin-Planck and the Clausius statements are, of course, equivalent. Demonstrations of this have been given frequently[4]. Mathematically, the statements may be expressed as

$$\oint \frac{\delta Q}{T} = 0 \tag{7.17}$$

obtained by integrating Eq.((5.2), over the cycle. This equation is commonly referred to as representing the *Clausius theorem.*

7.18 Alternative Formulations of the First and Second Laws

There are many alternative formulations of both laws. The ones that probably most beguile by their simplicity and immediate application to everyday life, are:

> *"You can't get anything for nothing"* or *"There is no free lunch"*

for the First Law, and

> *"What you get is less than what you expect"* or *"Life is tough"*

for the Second Law.

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[4] see, e.g., Blinder (1969), p.303; Zemansky (1958), p.185.

7.19 Statements of the Third Law

Although statements of the Third Law do not require the notion of a cyclic process, we include some of them here for completeness. Nernst originally formulated the Third Law in the words:

> *"The entropy of any system vanishes at zero temperature".*

This is also known as the *Nernst Heat Theorem* (§ 2.21). The statement, however, is not true in general. There are systems (e.g. certain macromolecular compounds) for which the entropy would not vanish at zero temperature even if the system were cooled infinitely slowly.

A wider definition of the Third Law states that

> *"The entropy of any finite system is* positive semi-definite *in the state for which* $T = 0$*".*

This statement is equivalent to Postulate V (cf. § 2.21) since, by §§ 3.3 and 3.5, the derivative $(\partial U/\partial S)|_{X(\neq S)}$ defines the thermodynamic temperature.

Another formulation states:

> *"It is impossible to reduce the temperature of any system to zero by any process in a finite number of steps".*

This is akin in form to the statements of the Second Law in § 7.17 in that it asserts the impossibility of a device or process. It expresses the *unattainability of absolute zero.* That this statement follows from the Nernst Heat Theorem has been shown, e.g., by Blinder (1969).

There are other statements of the Third Law, each emphasizing particular aspects. Among them are the formulations associated with the names of Planck, Simon, Fowler and Guggenheim, and others more.

7.20 Unsuitability of the Historic Laws of Thermodynamics as Postulates

A brief comment is in order here concerning the suitability of the so-called *laws of thermodynamics* as postulates for a systematic exposition of thermodynamic theory. The laws evolved historically, and not in the order in which they are numbered. The essentials leading to the Second Law were known before the First was generally appreciated. The Zeroth Law was added after the Third.

Formulation of these laws in precise mathematical language requires other thermodynamic concepts as already known. The statement of the Zeroth Law (§ 4.11) requires an understanding of the notion of thermal equilibrium. Similar difficulties arise in connection with the other laws.

The statement of the First Law contained in § 7.16 presupposes the notions of heat, work, and a thermodynamic cyclic operation. Poincaré's statement for a cyclic process can be recast as

$$\oint(\delta Q - \delta W) = 0\,. \tag{7.20}$$

In a general, non-cyclic process the (algebraic) sum of δQ and δW is, of course, not zero. We have [cf. Eq.$(2.6)_2$]

$$\delta W + \delta Q = dU \tag{7.20}$$

where δW is now the work done *on* the system. A generalization of the First Law of Thermodynamics thus *leads* to a definition of the internal energy . However, we would rather *start* with such a definition.

The Clausius Inequality, Eq.$(5.5)_1$, as well as the Clausius Theorem, Eq.(7.17) may be taken as mathematical expressions of the Second Law but they cannot be reconciled with the statements in § 7.17 without first introducing the concepts of entropy, temperature, and cyclic processes.

The formulations of the Third Law given in § 7.19 require the notion of entropy and temperature. With respect to that law it is now generally accepted that a true understanding of it can be achieved only in the framework of quantum mechanics which exceeds the scope of the present work.

We conclude that the historical laws do not form a postulatory basis for an exposition of the structure of the theory of equilibrium thermodynamics.

8. THERMODYNAMIC POTENTIALS

To understand the behavior of a thermodynamic system when one or more of its *intensive* parameters are held constant requires forms of the fundamental equation in which one or more of the extensive parameters are replaced by the conjugate intensive parameter *without loss of information.*

If these forms of the fundamental equation are derived in the *energy representation*, we refer to them as *alternative thermodynamic potentials* for reasons that will become clear in the first few sections to follow. These thermodynamic potentials, their derivation through the use of the Legendre transformation, their properties, and some closely related topics—in particular the Gibbs-Duhem equation and the degrees of freedom of a thermodynamic system—are the subject of this chapter.

In the *entropy representation* an analogous development defines the so-called *Massieu functions* that form the subject of the next chapter.

8.0 Chapter Contents

8.1 The Internal Energy as a Thermodynamic Potential

The internal energy, U, may be regarded as a *thermodynamic potential* for work, heat, or mass action. We recognize this when we examine the partial derivative of U with respect to the volume, V, or the entropy S, or the mole numbers, N_m, keeping all others constant. By §§ 3.3 and 3.6, in the energy representation the jth intensity parameter is

$$Y_j = \left.\frac{\partial U}{\partial X_j}\right|_{X(\neq X_j)} . \tag{8.1}$$

Let us now substitute for X in Eq.(8.1) the parameters V, S, N_m in turn.

8.2 The Internal Energy as a Potential for Work

Consider first a multicomponent simple system in which volume change is the only work. Taking the derivative with respect to the volume, we have, at constant entropy and mole numbers,

$$-P = \left.\frac{\partial U}{\partial V}\right|_{S,\ldots N\ldots} . \qquad (8.2)_1$$

Thus, by an analogy from mechanics, at constant entropy and constant mole numbers, the internal energy, U, may be considered a 'potential for work'. To see this more clearly, consider an isolated system in contact with a reversible work source (RWS). By the principle of the conservation of energy (Postulate II, § 2.4), since there is no change in either heat or mass action,

$$-dU = \delta W^{\mathrm{RWS}} . \qquad (8.2)_2$$

The decrease in internal energy therefore indeed represents the amount of work the simple system can deliver to a reversible work source in a reversible process at constant entropy and constant mole numbers.

8.3 The Internal Energy as a Potential for Heat

At constant volume and mole numbers, Eq.(8.1) becomes

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,\ldots N\ldots} , \qquad (8.3)_1$$

and, by Eq.$(8.3)_1$, U may equally be regarded as a 'potential for heat'. This time let the system be in contact with a reversible heat source (RHS). Since there is no change in either work or mass action,

$$-\,dU = \delta Q^{\mathrm{RHS}}\,, \tag{8.3$_2$}$$

and this is the decrease in internal energy representing the amount of heat the system can deliver to a reversible heat source in a reversible process at constant volume and constant composition.

8.4 The Internal Energy as a Potential for Mass Action

Finally, at constant volume, entropy, and all mole numbers except the mth,

$$\mu_{\mathrm{m}} = \left.\frac{\partial U}{\partial N_m}\right|_{S,\,V,\;N(\neq N_m)}\,, \tag{8.4$_1$}$$

and this shows U to be a 'potential for mass action' at constant entropy, volume, and mole numbers other than N_m. We now find

$$-\,dU = \delta M^{\mathrm{RMS}} \tag{8.4$_2$}$$

for the decrease in internal energy representing the amount of mass action the system can deliver to a reversible matter source (RMS) in a reversible process at constant entropy, volume, and the chosen constant mole number.

8.5 Alternative Thermodynamic Potentials

An alternative thermodynamic potential is a fundamental equation containing one or more intensive parameters as canonical variables. Such a fundamental equation cannot be obtained simply by replacing an extensive parameter by its conjugate intensive parameter. A simple replacement does not turn a fundamental equation into another one. Instead, it produces an equation of state, with an attendant loss of information.

Consider an example. Replacement of the entropy, S, in the fundamental equation for the physical simple system, $U = U(S,\,V)$, by its conjugate parameter, the temperature, T, gives $U = U(T,\,V)$, the differential form of which is

$$dU = \left.\frac{\partial U}{\partial T}\right|_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV\,. \tag{8.5}$$

This implies that $T = T(U,\,V)$, i.e., a functional dependence of T on U and V which, by § 3.11, is an equation of state. The replacement has thus resulted in a loss of information because T is a partial derivative of U (cf. § 3.12). Integration of Eq.(8.5) can therefore recover the fundamental equation only within an arbitrary constant of integration.

8.6 The Legendre Transformation

The appropriate device for generating alternative thermodynamic potentials without loss of information is the *Legendre transformation* (see Appendix 3). Each alternative thermodynamic potential leads to an alternative form of the fundamental equation with its own extremum principle, equilibrium and stability conditions, Gibbs equation, and Euler equation. Not all possible alternative potentials are in common use.

8.7 Number of Alternative Thermodynamic Potentials

We consider the number of alternative thermodynamic potentials that are possible for a given thermodynamic system. A system with n parameters (all of which are extensive) has as many alternative thermodynamic potentials as there are *partial*[5] Legendre transforms of the internal energy. By § A3.7 this number is $2^n - 2$. The *total* number of thermodynamic potentials includes the internal energy and is therefore $2^n - 1$, i.e., 1 more than the number of alternative potentials.

8.8 Degrees of Freedom

While the extensive parameters of a thermodynamic system are independent of each other, the conjugate intensive parameters are not (cf. § 8.22). The number of intensive parameters that are capable of independent variation is called the *number of degrees of freedom*, f, of the system. This number is 1 less than the number of extensive variables, i.e., $f = n - 1$. If the system is of *constant composition*, the number of degrees of freedom reduces by one and the number of alternative thermodynamic potentials is halved. If the system is composed of more than 1 component, the number of extensive variables is increased by 1 for each added component.

To illustrate: the single-component simple system with $U = U(S, V, N)$ has 3 extensive parameters, 2 degrees of freedom, 6 alternative, and a total number of 7 thermodynamic potentials. At *constant composition* the number of alternative potentials is halved because only the Legendre transformations that exclude the chemical potential, μ, are of interest. The total number of thermodynamic potentials then becomes 4.

8.9 The Primary Alternative Thermodynamic Potentials

We now proceed to introduce what we may call the *primary* alternative thermodynamic potentials, namely, the potentials of the single-component simple system at constant composition. The three new primary potentials (i.e., those in addition to U), are the *free energy*, F, the *enthalpy*, H, and the *free enthalpy*, G. These potentials are obtained as Legendre transforms involving the temperature and/or the pressure. For each of the new potentials we consider the work available when the respective intensive canonical variable or variables are held constant. We then state the extremum principle, the equilibrium and stability conditions, and the Gibbs and the Euler equations for each potential.

Brief reference will be made in §§ 8.19 and 8.21 to the potentials obtained through Legendre transformations including the chemical potential, μ.

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[5] The *complete* Legendre transform vanishes (see §§ 8.22 and A3.5)

8.10 The Free Energy

In a single-component simple system $U[T]$ is that Legendre transform of $U(S, V, N)$ in which the entropy, S, has been replaced by the temperature, T. The thermodynamic potential

$$F = U[T] = U - TS \qquad (8.10)_1$$

is called the *(Helmholtz) free energy* or *Helmholtz potential*[6]. The canonical variables of the free energy of a simple system are T, V, and $\ldots N_m \ldots$. Thus, we have the alternative fundamental equation of a multicomponent simple system in the *free energy representation*

$$F = F(T, V, \ldots N_m \ldots) \qquad (8.10)_2$$

and the Gibbs equation becomes

$$dF = -SdT - PdV + \sum\nolimits_m \mu_m dN_m \qquad (8.10)_3$$

in the same representation. The relations

$$-P = \left.\frac{\partial F}{\partial V}\right|_{T, \ldots N \ldots} \qquad (8.10)_4$$

and

$$\mu_m = \left.\frac{\partial F}{\partial N_m}\right|_{T, V, N(\neq N_m)} \qquad (8.10)_5$$

show that the free energy is a potential for work at constant temperature and composition, and one for mass action at constant temperature, volume, and mole numbers other than N_m.

Taking the total differential of $F = U - TS$ we see that at constant temperature the change in free energy is

$$dF = dU - TdS. \qquad (8.10)_6$$

Substituting for U in $F = U - TS$ from Eq.$(3.10)_4$ yields

$$F = -PV + \sum\nolimits_m \mu_m N_m \qquad (8.10)_7$$

as the alternative form of the Euler equation in the free energy representation.

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[6] The free energy is sometimes, particularly in the older literature, refered to as the *work content* and is then usually assigned the symbol A.

8.11 Work Available at Constant Temperature

The free energy represents the amount of work available from a closed simple system in contact with a reversible work source and with a heat reservoir. By Postulate II (§ 2.4), since in a closed system there is no change in mass action,

$$dU = -\delta W^{\text{RWS}} - \delta Q^{\text{HR}} \tag*{(8.11)$_1$}$$

where the work term has been given the negative sign because it is work delivered *by* the system *to* the reversible work source. Now, by § 6.3, $\delta Q^{\text{HR}} = T^{\text{HR}} dS^{\text{HR}}$ and, since the temperature is constant and the reversible work source is at constant entropy, we have $\delta Q^{\text{HR}} = 0$, and, hence,

$$-dF = -d(U - TS) = \delta W^{\text{RWS}}. \tag*{(8.11)$_2$}$$

This shows that, as asserted, the decrease in free energy equals the amount of work a closed system can deliver in a reversible process at constant temperature.

We may express this in another way by saying that F represents that part of the internal energy that can be transformed into work at constant temperature. It is thus the *free energy* while TS may be called the *bound energy* or the *isothermally unavailable energy.*

8.12 Extremum Principle, Equilibrium and Stability Conditions for the Free Energy

The extremum principle for the free energy states:

> *"At equilibrium the value of any unconstrained parameter of a system in diathermal contact with a heat reservoir is such that the free energy is minimized at constant temperature".*

By § 4.4) the conditions of equilibrium and stability for the free energy are

$$(dF)_T = 0 \quad \text{and} \quad (d^2F)_T > 0\,. \tag*{(8.12)}$$

For a process to proceed spontaneously at constant temperature we must therefore have $(dF)_T < 0$, i.e., the free energy of a system must decrease.

8.13 The Enthalpy

The alternative thermodynamic potential

$$H = U[P] = U + PV \tag*{(8.13)$_1$}$$

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[7] The enthalpy is sometimes referred to as the *heat content.*

is called the *enthalpy*[7]. Its canonical variables in a simple system are S, P, and $\ldots N_m \ldots$ We now have the fundamental equation of a multicomponent simple system in the *enthalpy representation*

$$H = H(S, P, \ldots N_m \ldots) \tag{8.13$_2$}$$

and the Gibbs equation

$$dH = TdS + VdP + \sum\nolimits_m \mu_m dN_m . \tag{8.13$_3$}$$

in the same representation. The relations

$$T = \left.\frac{\partial H}{\partial S}\right|_{P,\ \ldots N \ldots} \tag{8.13$_4$}$$

and

$$\mu_m = \left.\frac{\partial H}{\partial N_m}\right|_{S,\ P,\ N(\neq N_m)} \tag{8.13$_5$}$$

show that the enthalpy is a potential for heat at constant pressure and composition, and a potential for mass action at constant entropy, pressure, and mole numbers other than N_m.

At constant pressure the change in enthalpy is

$$dH = dU + PdV\ . \tag{8.13$_6$}$$

Substituting for U in $H = U + PV$ from Eq.(3.10)$_4$ yields

$$H = TS + \sum\nolimits_m \mu_m N_m \tag{8.13$_7$}$$

as the alternative form of the Euler equation in the enthalpy representation.

8.14 Work Available at Constant Pressure

The enthalpy represents the amount of work available from a closed simple system in contact with a reversible work source and a volume reservoir. Since there is neither heat flux nor mass action, we have

$$dU = -\delta W^{\mathrm{RWS}} - \delta W^{\mathrm{VR}}\ . \tag{8.14$_1$}$$

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[7] The enthalpy is sometimes referred to as the *heat content*.

But

$$\delta W^{\mathrm{VR}} = P^{\mathrm{VR}} dV^{\mathrm{VR}} \,, \tag{8.14$_2$}$$

and therefore

$$-\, dH = \,-\, d(U + PV) = \delta W^{\mathrm{RWS}} \,. \tag{8.14$_3$}$$

Thus, the decrease in enthalpy equals the amount of work a closed system can deliver in a reversible process at constant pressure.

In an arbitrary process both heat and work may be transferred to the system. If the latter is closed and is maintained at constant pressure, all but the first term on the right-hand side of Eq.(8.13)$_3$ vanish and we have

$$(dH)_{P,\dots N\dots} = TdS = \delta Q \tag{8.14$_4$}$$

by Eq.(5.3). Thus, heat added to a closed system at constant pressure appears as an increase in enthalpy.

8.15 Extremum Principle, Equilibrium and Stability Conditions for the Enthalpy

The extremum principle for the enthalpy states:

> *"At equilibrium the value of any unconstrained parameter of a simple system coupled with a volume reservoir through a movable wall is such that the enthalpy is minimized at constant pressure".*

The conditions of equilibrium and stability for the enthalpy become:

$$(dH)_P = 0 \qquad \text{and} \qquad (d^2H)_P > 0 \,. \tag{8.15}$$

For a process to proceed spontaneously at constant pressure we must therefore have $(dH)_P < 0$, i.e., the enthalpy of the system must decrease.

8.16 The Free Enthalpy

The alternative thermodynamic potential

$$G = U[T, P] = U - TS + PV = H - TS \tag{8.16$_1$}$$

is called the *free enthalpy* or *Gibbs free energy* or *Gibbs potential*. Its canonical variables in a simple system are T, P, and $\dots N_m \dots$

We obtain the fundamental equation in the *free enthalpy representation* as

$$G = G(T,\, P,\, \ldots N_m \ldots) \tag{8.16$_2$}$$

and the Gibbs equation as

$$dG = -SdT + VdP + \sum\nolimits_m \mu_m dN_m \tag{8.16$_3$}$$

in the same representation. The relation

$$\mu_m = \left.\frac{\partial G}{\partial N_m}\right|_{T,\,P,\,N(\neq N_m)} \tag{8.16$_4$}$$

shows that the free enthalpy is a potential for mass action at constant temperature, pressure, and mole numbers other than N_m.

At constant temperature and pressure the change in free enthalpy is

$$dG = dU - TdS + PdV\,. \tag{8.16$_5$}$$

Substituting for U in $G = U - TS + PV$ from Eq.(3.10)$_4$ yields the Euler equation as

$$G = \sum\nolimits_{\mathrm{m}} \mu_{\mathrm{m}} N_{\mathrm{m}}. \tag{8.16$_6$}$$

The Euler equation of a multicomponent simple system in the free enthalpy representation thus consists of the mass action terms only.

Equations (8.16)$_4$ and (8.16)$_6$ are valid only for simple thermodynamic systems. In non-simple systems other alternative potentials assume the role of the free enthalpy [see § 8.25 and the Introduction to Chapter 17; specifically, compare the two equations Eqs.(8.16)$_4$ and (8.16)$_6$ with Eqs.(17.10)$_3$ and (17.5)$_{4.7}$].

8.17 Work Available at Constant Temperature and Pressure

The free enthalpy represents the amount of work available from a closed simple system in contact with a reversible work source and a heat reservoir as well as a volume reservoir. By arguments analogous to those used in §§ 8.11 and 8.14, we have

$$-dG = -d(U - TS + PV) = -d(H - TS) = \delta W^{\mathrm{RWS}}\,. \tag{8.17}$$

Thus, the decrease in free enthalpy equals the amount of work a closed simple system can deliver in a reversible process at constant temperature and pressure.

Expressing this again in another way we may say that G represents that part of the internal energy that can be transformed into work at constant temperature and pressure.

Alternatively, it is that part of the *enthalpy* that can be transformed into work at constant temperature. It is thus the *free enthalpy* while TS may be called the *bound enthalpy* or the *isothermally unavailable enthalpy.* The term 'free enthalpy' thus appears preferable to the alternate terms *Gibbs free energy* or *Gibbs potential.*

8.18 Extremum Principle, Equilibrium and Stability Conditions, for the Free Enthalpy

The extremum principle for the free enthalpy states:

> *"At equilibrium the value of any unconstrained parameter of a system coupled with a heat reservoir through a diathermal wall and with a volume reservoir through a movable wall is such that the free enthalpy is minimized at constant temperature and pressure".*

The conditions of equilibrium and stability for the free enthalpy become:

$$(dG)_{T,P} = 0 \qquad \text{and} \qquad (d^2G)_{T,P} > 0\,. \tag{8.18}$$

For a process to proceed spontaneously at constant temperature and pressure we must therefore have $(dG)_{T,P} < 0$, i.e., the free enthalpy of the system must decrease.

8.19 The Grand Canonical Potential

The potential

$$J = U[T,\mu_m] = U - TS - \mu_m N_m = -PV\,, \tag*{(8.19)$_1$}$$

called the *grand canonical potential for the mth component,* is a potential for open systems. Its canonical variables are T, V, and μ_m.

The Gibbs equation of the grand canonical potential of a single-component simple system becomes

$$dJ = -SdT + PdV - \mu dN\,. \tag*{(8.19)$_2$}$$

The grand canonical potential has found use in statistical mechanics.

8.20 The Extremum Principle, Equilibrium and Stability Conditions for the Grand Canonical Potential

The extremum principle for the grand canonical potential states:

> *"At equilibrium the value of any unconstrained parameter of a single component simple system coupled with a heat reservoir through a diathermal wall and with a matter reservoir through a semi-permeable*

barrier is such that the grand canonical potential is minimized at constant temperature and the chemical potential.

The conditions of equilibrium and stability for the grand canonical potential become:

$$(dJ)_{T,\mu} = 0 \qquad \text{and} \qquad (d^2J)_{T,\mu} > 0\,. \tag{8.20}$$

For a process to proceed spontaneously at constant temperature and pressure we must therefore have $(dJ)_{T,\mu} < 0$, i.e., the grand canonical potential of the system must decrease.

8.21 Other Thermodynamic Potentials of the Simple Systems

Of the six partial Legendre transforms of the internal energy of a single-component simple system the first-order transform,

$$U[\mu] = TS - PV, \qquad (8.21)_1$$

and the remaining second-order transform,

$$U[P, \mu] = TS, \qquad (8.21)_2$$

have not received separate symbols or names. In a multicomponent simple system we also have the additional transforms $U[\mu_m]$, $U[T, \mu_m]$, and $U[P, \mu_m]$

8.22 The Gibbs-Duhem Equation

The complete Legendre transformation of the internal energy replaces all canonical variables (i.e., extensive parameters) of the system by their conjugate intensive parameters in the energy representation. But the complete Legendre transform of any system vanishes (cf. § A3.5). The resulting differential equation linking the intensive variables of the system,

$$\sum_j Y_j\, dX_j = 0\,, \qquad (8.22)_1$$

is called the *Gibbs-Duhem equation.*

As an example, the complete Legendre transform of a single-component simple system is

$$U[T, P, \mu] = U - TS + PV - \mu N \qquad (8.22)_2$$

But, substituting for U from the Euler equation, Eq.(3.10)$_4$, we find that

$$U[T, P, \mu] = 0\,, \qquad (8.22)_3$$

and thus Eq.(8.22)$_1$ yields

$$SdT - VdP + Nd\mu = 0 \qquad (8.22)_4$$

as the Gibbs-Duhem equation of the single-component simple system. For a multi-component simple system the equation takes the form

$$SdT - VdP + \sum_m N_m \, d\mu_m = 0 \, . \qquad (8.22)_5$$

We infer that the Gibbs-Duhem equation of any system, including any non-simple system, establishes a similar relation between the system's intensive parameters.

8.23 Significance of the Gibbs-Duhem Equation

The Gibbs-Duhem equation represents an important relation between the intensive parameters, Y_k, of a system. Since the Y_k are all connected through this equation, they are not independent of each other (cf. § 8.8). The integrated form of the equation can therefore be used to find explicit expressions for the chemical potential.

8.24 The Chemical Potential Revisited

Taking the partial derivative with respect to N in the appropriate forms of the Gibbs equation of a single component simple system, i.e., Eqs. $(3.10)_3$, $(8.10)_3$, $(8.13)_3$, and $(8.16)_3$, we find

$$\left.\frac{\partial U}{\partial N}\right|_{S,V} = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \left.\frac{\partial H}{\partial N}\right|_{S,P} = \left.\frac{\partial G}{\partial N}\right|_{T,P} = \mu . \qquad (18.24)$$

In other words, the derivative of any of the thermodynamic potentials with respect to the mole number (the amount of material) equals the chemical potential. Thus the chemical potential occupies a special position among the other intensive parameters of the system: it allows us to calculate the change in any of the thermodynamic potentials with a change in the amount of material.

Equation (8.24) is easily extended to multicomponent simple systems. The partial derivatives then take the forms exemplified by Eqs. $(8.4)_1$, $(8.10)_5$, $(8.13)_5$, and $(8.16)_4$.

8.25 Thermodynamic Potentials in Non-Simple Systems

Hitherto we have considered only the so-called simple systems in which the PV term is the only work term allowed. If work terms other than PV are to be accommodated, then the Gibbs equation for a single component non-simple system in the energy representation takes the form

$$dU = TdS - PdV + \sum_p Y_p \, dX_p + \mu dN \qquad (8.25)$$

where the Y_pX_p are the added work terms in which the Y_p are the intensive, and the X_p are the extensive parameters. We must then define new thermodynamic potentials with the help of the appropriate Legendre transformations. An example of this is discussed in Chapter 17. The formalism can be extended to systems in which surface effects cannot be neglected or which are acted on, e.g., by electrical, magnetic, or gravitational fields. Unfortunately the number of definable thermodynamic potentials increases rapidly with the number of work terms considered.

9. MASSIEU FUNCTIONS

A Legendre transformation resulting in the replacement of one ore more extensive variables by the conjugate intensive variable in the *entropy representation* defines a *Massieu function.* We consider here only the Massieu functions for a single-component simple system. The intensive parameters of this system in the entropy representation are $1/T$, P/T, and μ/T. Extension to multicomponent simple systems is straightforward. There is no general agreement on the symbols and names for the Massieu functions. We assign non-italic uppercase Greek letters to them in this text.

Massieu functions are useful in manipulations based on the entropy representation. Thus, they find application in irreversible thermodynamics and in statistical mechanics. In this text, two of the Massieu functions serve in deriving the stability criteria in the entropy representation (§ 18.14).

9.0 Chapter Contents

9.1 Massieu Functions from First-Order Legendre Transformations

By § 8.7 there are 6 Legendre transforms, hence 6 Massieu functions, for the single-component simple system. We start by listing the Massieu functions obtained from the first-order Legendre transforms of the base function, $S = S(U, V, N)$ for that system in the entropy representation. We recall the Euler equation in the entropy representation

$$S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}N \, . \qquad (9.1)_1$$

Let the first of the Massieu functions be

$$\Psi = S\left[\frac{1}{T}\right] = S - \frac{1}{T}U \qquad (9.1)_2$$

which is often called *THE Massieu function.* Its differential form is

$$d\Psi = dS\left[\frac{1}{T}\right] = -U\,d\frac{1}{T} + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN \, . \qquad (9.1)_3$$

The next two Massieu functions of the single-component simple system are

$$\Xi = S\left[\frac{P}{T}\right] = S - \frac{P}{T}V \qquad (9.1)_4$$

with

$$d\Xi = dS\left[\frac{P}{T}\right] = \frac{1}{T}\,dU - V\,d\frac{P}{T} - \frac{\mu}{T}\,dN\,, \qquad (9.1)_5$$

and

$$\Theta = S\left[\frac{\mu}{T}\right] = S + \frac{\mu}{T}N\,, \qquad (9.1)_6$$

with

$$d\Theta = dS\left[\frac{\mu}{T}\right] = \frac{1}{T}\,dU + \frac{P}{T}\,dV + N\,\frac{d\mu}{T}\,. \qquad (9.1)_7$$

The last two functions are unnamed.

9.2 Massieu Functions from Second-order Legendre Transformations

Of the three Massieu functions for the single-component simple system resulting from second-order Legendre transformations, the function

$$\Phi = S\left[\frac{1}{T}, \frac{P}{T}\right] = S - \frac{1}{T}\,U - \frac{P}{T}\,V \qquad (9.2)_1$$

with

$$d\Phi = dS\left[\frac{1}{T}, \frac{P}{T}\right] = -U\,d\frac{1}{T} - V\,d\frac{P}{T} - \frac{\mu}{T}dN \qquad (9.2)_2$$

is often called the *Planck function.* The function

$$\Omega = S\left[\frac{1}{T}, \frac{\mu}{T}\right] = S - \frac{1}{T}U + \frac{\mu}{T}\,N \qquad (9.2)_3$$

with

$$d\Omega = dS\left[\frac{1}{T}, \frac{\mu}{T}\right] = -U\,d\frac{1}{T} + \frac{P}{T}\,dV + N\,d\frac{\mu}{T} \qquad (9.2)_4$$

is sometimes called the *Kramer function.* Finally, we have the unnamed function

$$\Gamma = S\left[\frac{P}{T}, \frac{\mu}{T}\right] = S - \frac{P}{T}\,V + \frac{\mu}{T}\,N \qquad (9.2)_5$$

with

$$d\Gamma = dS\left[\frac{P}{T}, \frac{\mu}{T}\right] = \frac{1}{T}\,dU - V\,d\frac{P}{T} + N\,d\frac{\mu}{T}\,. \tag{9.2$_6$}$$

9.3 The Gibbs-Duhem Equation in the Entropy Representation.

For the single-component simple system the third order Legendre transformation is a complete transformation. There is thus only one such Massieu function and this is the Gibbs-Duhem equation in the entropy representation. We obtain it as

$$U\,d\frac{1}{T} + V\,d\frac{P}{T} - N\,d\frac{\mu}{T} = 0 \tag{9.3}$$

and this may be compared with its form in the energy representation, Eq.$(8.22)_4$.

Equation (9.3) is a relation between the I_k, the intensive parameters of the single component simple system in the entropy representation, $1/T$, P/T, and μ/T, just as Eq.$(8.22)_4$ is a relation between the intensive parameters, T, P, and μ, of the single component simple system in the energy representation.

Extending this to the multicomponent simple system and to non-simple systems alike, avers that the intensive parameters in the entropy representation are not independent of each other (cf. § 8.23).

9.4 Relation of the Massieu Functions to the Thermodynamic Potentials

The Massieu functions bear simple relations to the thermodynamic potentials although the relations are not immediately obvious for all. They are, however, readily obtained. For convenience, we recall the Euler equation in the energy representation,

$$U = TS - PV + \mu N\,. \tag{9.4$_1$}$$

Then

$$\Psi = -\frac{U - TS}{T} = -\frac{F}{T}, \tag{9.4$_2$}$$

by Eq.$(8.10)_1$,

$$\Xi = \frac{TS - PV}{T} = \frac{U - \mu N}{T} = \frac{U[\mu]}{T}, \tag{9.4$_3$}$$

by Eq.$(8.21)_1$,

$$\Theta = \frac{TS + \mu N}{T} = \frac{U + PV}{T} = \frac{H}{T}, \tag{9.4$_4$}$$

by Eq.(8.13)$_7$,

$$\Phi = -\frac{U - TS + PV}{T} = -\frac{G}{T}, \qquad (9.4)_5$$

by Eq.(8.16)$_1$,

$$\Omega = -\frac{U - TS - \mu N}{T} = -\frac{PV}{T} = \frac{J}{T}, \qquad (9.4)_6$$

by Eq.(8.19)$_1$, and finally

$$\Gamma = \frac{TS - PV + \mu N}{T} = \frac{U}{T}. \qquad (9.4)_7$$

by Eq.(3.10)$_4$.

We complete the pattern by noting that

$$S = \frac{U[P, \mu]}{T} \qquad (9.4)_8$$

by Eq.(8.21)$_2$.

9.5 The Extremum Principles for the Massieu Functions

While a thermodynamic potential is *minimized* at equilibrium for constant values of its intensive canonical variable(s), a Massieu function is *maximized* under the same conditions. This is easy to see in case of the Ψ and Φ functions. Equations (9.4)$_2$ and (9.4)$_5$ indeed show that Ψ is maximized when F is minimized at constant temperature, and that Φ is maximized when G is minimized at constant temperature and pressure. However, maximization of Ξ requires that P/T be maximized while $1/T$ is varied. Thus, although the principle is valid in theory, its experimental realization may be quite difficult, if not impossible.

10. SECOND-ORDER PARTIAL DERIVATIVES

In § 3.3 we introduced the intensive parameters as the *first-order* partial derivatives of the internal energy. The *second-order* partial derivatives are no less important. A system having n extensive variables and, hence, $\mathrm{f} = n - 1$ degrees of freedom (cf. § 8.8), has a total of $\mathrm{f} + 1 = n$ first order, and a total of $\frac{1}{2}(\mathrm{f}+1)(\mathrm{f}+2) = n(n+1)/2$ *distinct* second-order partial derivatives of the internal energy. Since the order in which the differentiation is carried out does not affect the value of a 'mixed' partial derivative, such derivatives are equal and are not counted separately in the stated total number. The equivalence of the mixed partial derivatives gives rise to a set of important relations known as the *Maxwell relations*.

Second-order partial derivatives may be derived from thermodynamic potentials other than the internal energy. Accordingly, we distinguish several sets of such derivatives.

10.0 Chapter Contents

10.1 The Fundamental Set

We consider the second-order partial derivatives of the simplest thermodynamic system[8], the *physical simple system* (cf. § 1.9), for which $U = U(S, V)$. It has thus a single degree of freedom and, hence, two first-order, and three second-order partial derivatives. The first-order derivatives are

$$\left.\frac{\partial U}{\partial S}\right|_V = T \qquad \text{and} \qquad \left.\frac{\partial U}{\partial V}\right|_S = -P,$$

and the three second-order ones take the forms

$$\left.\frac{\partial^2 U}{\partial S^2}\right|_V, \qquad \left.\frac{\partial^2 U}{\partial V \partial S}\right|_S = \left.\frac{\partial^2 U}{\partial S \partial V}\right|_V, \qquad \left.\frac{\partial^2 U}{\partial V^2}\right|_S.$$

Making use of the first partial derivatives, the second ones become

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[8] For an example of a more complex system see Chapter 17.

$$\left.\frac{\partial T}{\partial S}\right|_V, \qquad \left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V, \qquad -\left.\frac{\partial P}{\partial V}\right|_S.$$

These derivatives are normally used in the form of their reciprocals

$$\left.\frac{\partial S}{\partial T}\right|_V = C_V/T \tag{10.1$_1$}$$

$$\left.\frac{\partial V}{\partial T}\right|_S = -\left.\frac{\partial S}{\partial P}\right|_V = \alpha_S V \tag{10.1$_2$}$$

$$-\left.\frac{\partial V}{\partial P}\right|_S = \kappa_S V \tag{10.1$_3$}$$

where C_V is the *heat capacity at constant volume* (the *isochoric* heat capacity), α_S is the *adiabatic expansivity*, and κ_S is the *adiabatic compressibility*. We call this set of second-order partial derivatives the *fundamental set*.

The useful relation

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V \tag{10.1$_4$}$$

follows from Eq.(10.1)$_1$ because in the physical simple system $dU = TdS - PdV$ [cf. Eq.(3.10)$_1$].

10.2 The Primary Set

In the derivatives just introduced the variables held constant were the extensive parameters. A corresponding set of derivatives in which the intensive parameters are kept constant, is obtained by using the free enthalpy, G, instead of the internal energy, U, as the basis of the derivation. For the physical simple system we have $G = G(T, P)$ and obtain

$$\left.\frac{\partial G}{\partial T}\right|_P = -S \qquad \text{and} \qquad \left.\frac{\partial G}{\partial P}\right|_{\mathrm{T}} = V$$

for the first, and

$$\left.\frac{\partial^2 G}{\partial T^2}\right|_P, \qquad \left.\frac{\partial^2 G}{\partial P \partial T}\right|_T = \left.\frac{\partial^2 G}{\partial T \partial P}\right|_P, \qquad \left.\frac{\partial^2 G}{\partial P^2}\right|_T$$

for the second-order derivatives. Making use of the first derivatives again, we find

$$-\left.\frac{\partial S}{\partial T}\right|_P, \qquad -\left.\frac{\partial S}{\partial P}\right|_T = \left.\frac{\partial V}{\partial T}\right|_P, \qquad -\left.\frac{\partial V}{\partial P}\right|_T .$$

Again we use their reciprocals in the form

$$\left.\frac{\partial S}{\partial T}\right|_P = C_P/T \qquad (10.2)_1$$

$$\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T = \alpha_P V \qquad (10.2)_2$$

$$-\left.\frac{\partial V}{\partial P}\right|_T = \kappa_T V \qquad (10.2)_3$$

where C_P is the *heat capacity at constant pressure* (the *isobaric* heat capacity), α_P is the *isobaric expansivity*, and κ_T is the *isothermal compressibility*.

The new second-order partial derivatives can all be expressed in terms of the fundamental set. They are, however, of primary importance experimentally. We therefore call this set the *primary set*.

Since $dH = TdS + VdP$ by Eq.(8.13)$_3$, we have

$$C_P = \left.\frac{\partial H}{\partial T}\right|_P \qquad (10.2)_4$$

in analogy to Eq.(10.1)$_4$.

10.3 Relations between the Fundamental and the Primary Sets

Some useful relations can be established between the members of the fundamental and the primary sets of the second-order partial derivatives. First we define the *heat capacity ratio* as

$$\gamma = C_P/C_V = c_P/c_V \qquad (10.3)_1$$

where $c_P = C_P/N$ and $c_V = C_V/N$ are the *molar heat capacities*. We then have

$$C_P/C_V = \kappa_T/\kappa_S = 1 - \alpha_P/\alpha_S \qquad (10.3)_2$$

i.e., the ratio is equal to the ratio of the compressibilities and is also simply related to the ratio of the expansivities.

The *heat capacity difference* is usually given in the form

$$C_V = C_P - TV\alpha_P^2/\kappa_T \, . \tag{10.3)$_3$}$$

These relations are derived in Appendix 2

10.4 'Hybrid' Sets

The fundamental and primary sets of second-order partial derivatives of the physical simple system were derived from $U = U(S,\, V)$, and $G = G(T,\, P)$, respectively. In the first, the canonical variables were the extensive parameters. In the second, they were the intensive ones. Second-order partial derivatives may be obtained also from the alternative thermodynamic potentials, the free energy, $F = F(T, V)$, and the enthalpy, $H = H(S, P)$. These derivations form *'hybrid'* sets whose canonical variables comprise both extensive and intensive parameters. A new coefficient is obtained only from the mixed second-order partial derivatives of these potentials. We have :

$$-\left.\frac{\partial^2 F}{\partial T \partial V}\right|_V = \left.\frac{\partial P}{\partial T}\right|_V = \gamma_V = \left.\frac{\partial^2 F}{\partial V \partial T}\right|_T = \left.\frac{\partial S}{\partial V}\right|_T \tag{10.4)$_1$}$$

and

$$\left.\frac{\partial^2 H}{\partial S \partial P}\right|_P = \left.\frac{\partial V}{\partial S}\right|_P = 1/\gamma_V = \left.\frac{\partial^2 H}{\partial P \partial S}\right|_S = \left.\frac{\partial T}{\partial P}\right|_S \, . \tag{10.4)$_2$}$$

where γ_V is the *isochoric (constant volume) pressure-temperature coefficient.* Its experimental determination from $(\partial P/\partial T)_V$ gives access to the other three derivatives above that are difficult to obtain experimentally because they require manipulation of the entropy, S.

10.5 Reduction of Partial Derivatives to the Primary Set

It is often desirable to express a given partial derivative in terms of the members of the experimentally more convenient primary set or, in other words, in terms of the parameters C_P, α_P, and κ_T. Reduction of a derivative in this way is equivalent to a coordinate transformation in thermodynamic configuration space to the canonical variables of the free enthalpy, T, P, ... (cf. Eqs.10.2).

Several methods have been proposed for the reduction of partial derivatives to the primary set. Callen (1963) describes a method of elimination based on the Maxwell relations that form the topic of §10.6.

Another method is due to Bridgman. Bridgman (1914, 1961) constructed a table containing the numerators and the denominators of the partial derivatives occurring in the thermodynamics of the physical simple system in the form $(\partial x)_y$. A typical example illustrating the use of Bridgman's table follows. Suppose we wish to reduce the so-called Joule-Thompson coefficient, $(\partial T/\partial P)_H$ [cf. Eq.(A2.3)$_{16}$]. Then

$$\left.\frac{\partial T}{\partial P}\right|_H = \frac{(\partial T)_H}{(\partial P)_H} = \frac{V - TV\alpha_P}{-C_P} = \frac{V(T\alpha_P - 1)}{C_P} \qquad (10.5)_1$$

where $(\partial T)_H$ and $(\partial P)_H$ are taken from the table. This is certainly the simplest method. Unfortunately, for any thermodynamic system with more than one degree of freedom the table would have to be quite large and apparently no extended table has ever been published.

A convenient transformation of derivatives is based on the use of Jacobians. The method consists in rewriting the derivative as a Jacobian, multiplying both the numerator and the denominator by $\partial(T, P, \ldots N \ldots)$, and rearranging. As an example, consider the constant volume pressure-temperature coefficient introduced in the preceding paragraph. We have

$$\gamma_V = \left.\frac{\partial P}{\partial T}\right|_V = \frac{\partial(P,V)}{\partial(T,P)} \cdot \frac{\partial(T,P)}{\partial(T,V)} = -\left.\frac{\partial V}{\partial T}\right|_P \cdot \left.\frac{\partial P}{\partial V}\right|_T = \alpha_P/\kappa_T\,. \qquad (10.5)_2$$

10.6 The Maxwell Relations

The relations equating the mixed second-order partial derivatives are known as the *Maxwell relations*. These important relations often allow the substitution of a derivative which is measured with relative ease in one experiment, for a derivative which is difficult, if not impossible, to determine in another. A system with f degrees of freedom has $\frac{1}{2}\mathrm{f}(\mathrm{f}+1)$ mixed second-order partial derivatives—and, therefore, Maxwell relations—for every one of the thermodynamic potentials. Since the total number of thermodynamic potentials is $2^{\mathrm{f}+1} - 1$ (cf. § 8.7), the total number of Maxwell relations for f degrees of freedom is $\frac{1}{2}\mathrm{f}(\mathrm{f}+1)(2^{\mathrm{f}+1} - 1)$.

The single-component simple system has 2 degrees of freedom. Of its 21 Maxwell relations we list those that are derived from the thermodynamic potentials U, H, F, and G since only these are in common use. The four potentials are displayed in bold font in the left margin.

$\boldsymbol{U}$:

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial P}{\partial S}\right|_{V,N}, \qquad \left.\frac{\partial T}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial S}\right|_{V,N}, \qquad -\left.\frac{\partial P}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial V}\right|_{S,N} \qquad (10.6)_1$$

$\boldsymbol{F}$:

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}, \qquad -\left.\frac{\partial S}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial T}\right|_{V,N}, \qquad -\left.\frac{\partial P}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial V}\right|_{T,N} \qquad (10.6)_2$$

H:

$$\left.\frac{\partial T}{\partial P}\right|_{S,N} = \left.\frac{\partial V}{\partial S}\right|_{P,N}, \qquad \left.\frac{\partial T}{\partial N}\right|_{S,P} = \left.\frac{\partial \mu}{\partial S}\right|_{P,N}, \qquad \left.\frac{\partial V}{\partial N}\right|_{S,P} = \left.\frac{\partial \mu}{\partial P}\right|_{S,N} \qquad (10.6)_3$$

G:

$$-\left.\frac{\partial S}{\partial P}\right|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{P,N}, \qquad -\left.\frac{\partial S}{\partial N}\right|_{T,P} = \left.\frac{\partial \mu}{\partial T}\right|_{P,N}, \qquad \left.\frac{\partial V}{\partial N}\right|_{T,P} = \left.\frac{\partial \mu}{\partial P}\right|_{T,N} (10.6)_4$$

Of these, the first of Eqs.$(10.6)_1$ and $(10.6)_4$ were introduced before as the reciprocals of Eqs.$(10.1)_2$ and $(10.2)_2$, while the first of Eqs.$(10.6)_2$ and $(10.6)_3$ are non others than Eqs.$(10.4)_1$ and $(10.4)_2$, respectively. These 'first' equations are particularly important because they allow us to determine hard-to-measure variations involving the entropy, in terms of the expansivities and the isochoric pressure-temperature coefficient.

10.7 Corresponding Members of a Maxwell Relation

Let us consider the number of possible Maxwell relations in general. For the single-component simple system ($f = 2$) there are altogether 21 Maxwell relations. For a binary simple system ($f = 3$) the number of possible Maxwell relations rises to 90.

Clearly, we need a method for enabling us to find—given a mixed second-order derivative—the corresponding member of the Maxwell relation whenever it is required. A method to do this may be found in Appendix A2 on Jacobians. The necessary relations are tabulated in § A2.2, part (5). An example is given in § A2.3, part (1).

11. IDEAL SYSTEMS

The first ten chapters of this text established the armamentarium necessary to describe the fundamental features of the phenomenological theory of equilibrium thermodynamics. This chapter introduces concepts underlying *idealized* (or simply *ideal*) *thermodynamic systems.* The next six chapters then discuss several such systems:

- the ideal gas,
- the monatomic ideal gas,
- the ideal mixture,
- the multicomponent ideal gas,
- the ideal solution,
- the ideal rubber.

Focusing particular attention on the *single-component* ideal gas, the first of the next chapters describes more generally the features shared by all ideal gases. The chapter on the ideal mixture discusses features common to the *multicomponent* ideal gas and to the ideal solution. The behavior of the three ideal gas systems underlie the behavior of real gases. Similarly, the ideal solution and the ideal rubber model the behavior of real solutions and real rubbers. The ideal solution and the ideal rubber are examples of a liquid and a solid system, respectively.

11.0 Chapter Contents

11.1 Idealized Systems

The idealized systems to be discussed in the following six chapters are model systems in the sense of the motto heading the Preface. Thus, they are not, in general, directly applicable to any real physical system. They do, however, model the basic features of such systems. Real physical systems generally show deviations from the behavior predicted by the idealized models. Much ingenuity has been devoted to the development of improvements to account for the behavior of real systems. While extremely important in practice, these improvements do not, however, present anything new from the viewpoint of the basic structure of the theory of thermodynamic behavior and, therefore, are outside the scope of this text.

11.2 Ideal Behavior

For the purposes of this text a necessary (but not necessarily sufficient) condition for ideal behavior is that the contributions of the extensive parameters in the fundamental equation be separable at constant composition. Putting this another way:

> *"The fundamental equation of an ideal system consists of additive terms, every one of which depends only on a single extensive variable aside from compositional variables such as the mole numbers".*

This feature characterizes all six of the systems mentioned above.

It further follows that, at constant composition, each equation of state of an ideal system—excepting the one involving the chemical potential—depends on only one of the extensive variables of the system..

11.3 Criteria for Ideal Behavior

Sufficient conditions for ideal behavior are conveniently formulated in terms of the intensive parameters since these do not depend on the size of the system. They are linked by the Gibbs-Duhem equation [cf Eq.(8.22)$_1$]. We may thus express the sufficient condition for the ideal behavior of a system by specifying the functional dependence of the chemical potential on the other intensive parameters. For the single-component general ideal gas and for the monatomic ideal gas the intensive parameters are T, P and. Hence, for these systems the implicit form of the sufficient condition becomes

$$\mu = \mu(T, P)\,. \tag{11.3)$_1$}$$

For the ideal mixture, the multicomponent ideal gas, and the ideal solution, this relation becomes

$$\mu_i = \mu_i(T, P, \overline{n}_i) \tag{11.3)$_2$}$$

because the chemical potential of the ith component depends on the composition. The latter is taken into account by including the intensive compositional variable, $\overline{n}_i$, i.e., the ith mole fraction (cf. § 14.5). The criteria for ideal behavior are then obtained by making the two implicit relations above explicit for each of the systems considered (cf. §§ 12.12, 13.10, 14.7, 15.12, 16.4 and 17.16).

11. 4 Domain of Validity

The systems listed at the beginning of this chapter are *model systems*. It is in the nature of a model that it bears no one-to-one correspondence to that which it models. The set of properties assigned to every model define its *domain of validity* within which it comes arbitrarily close to the reality that underlies it. The domain of validity does not need to be stated explicitly. However, when using a model, the user must always be aware of its domain of validity and of its limitations outside of this domain. The monatomic ideal gas furnishes a perfect example (see § 13.9).

12. THE IDEAL GAS

The two extreme idealized thermodynamic systems are the ideal gas and the perfect crystal. In the first the arrangement of molecules (or atoms) is completely random, in the second it is perfectly ordered. The thermodynamic properties of an *ideal gas* are particularly instructive because of their relative simplicity. The simplest ideal gas is the *monatomic ideal gas* which will be discussed in the next chapter. Any real gas, monatomic or not, approximates the behavior of an ideal gas in the limit that $T \rightarrow \infty$ and $P \rightarrow 0$.

12.0 Chapter Contents

12.1 The Fundamental Equation of the Ideal Gas in the Entropy Representation

Although thermodynamic theory does not depend on the existence of an explicit form of the fundamental equation (cf. § 3), it is, nevertheless, useful to learn how the theory applies when such a fundamental equation is available. The ideal gas presents us with the opportunity of studying the properties of a rather simple fundamental equation. The ideal rubber offers another such opportunity (cf. § 17.15).

The fundamental equation of an ideal gas cannot be derived within phenomenological thermodynamic theory. It can be obtained, however, in the entropy representation from a complete set of the equations of state (cf. § 12.3), and can also be derived with the help of classical statistical mechanics and quantum mechanics. Appendix 4 gives a short account of the derivation of the (molar) fundamental equation of the single-component ideal gas in the entropy representation. It leads to

$$s = s(u, v) = s_o + f(u) + R\ ln\ v/v_o \qquad (12.1)_I$$

where R is the *universal gas constant*, $s = S/N, u = U/n, v = V/N$, and the subscript 'o' denotes a suitably chosen *reference state*. Equation $(12.1)_I$ contains no term which depends simultaneously on both u and v and thus satisfies the requirement for ideal behavior as formulated in § 11.2. The function $f(u)$ is a function of u only. Its explicit form differs from gas to gas but it will always be such that $f(u_o) = 0$. Because $f(u)$ is not known explicitly in general, Eq.(12.1)$_1$ cannot be solved for the molar fundamental equation in the energy representation, $u = u(s, v)$.

In terms of the mole number, N, Eq.(12.1)$_1$ becomes

$$S = N\frac{S_o}{N_o} + Nf(U/N) + N\mathrm{R}\, ln\, \frac{VN_o}{V_oN} \tag*{(12.1)$_2$}$$

as the general form of the fundamental equation of a single-component ideal gas in the entropy representation. In the remainder of this chapter 'ideal gas' will refer to a single-component ideal gas unless otherwise stated.

12.2 The Equations of State of the Ideal Gas in the Entropy Representation

Because we have no explicit fundamental equation of the ideal gas in the energy representation, we derive the three equations of state of the ideal gas in the entropy representation. For the first equation we find

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N} = N\frac{df(U/N)}{dU} = \frac{df(u)}{du} \tag*{(12.2)$_1$}$$

from Eq.(3.11)$_{4.1}$. Although, in the absence of an explicit differentiable function of U, the differentiation could only be indicated, Eq.(12.2)$_1$ shows that the internal energy depends—apart from the mole number, N—*only* on the temperature, T. This exclusive dependence of the internal energy on the temperature is an important characteristic of the ideal gas and allows us to express the first equation of state of the ideal gas in the form

$$\frac{1}{T} = \frac{cN\mathrm{R}}{U} = \frac{c\mathrm{R}}{u} \tag*{(12.2)$_2$}$$

where c is a dimensionless constant (see the introduction to Chapter 13).

The second equation of state follows from Eq.(3.11)$_{4.1}$ as

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} = \frac{N\mathrm{R}}{V} = \frac{\mathrm{R}}{v}. \tag*{(12.2)$_3$}$$

This is commonly written as

$$PV = N\mathrm{R}T \qquad \text{or} \qquad Pv = \mathrm{R}T \tag*{(12.2)$_4$}$$

and has the same form for *all* ideal gases including the multicomponent ideal gas (cf. § 15.3). The second equation of state is sometimes referred to simply as *THE* equation of state of the ideal gas or *THE ideal gas equation of state.*

Introducing the equations $U = cN\mathrm{R}T$ and $PV = N\mathrm{R}T$ into $H = U + PV$ it is seen at once that the enthalpy of an ideal gas also depends only on the temperature apart from the mole number, N.

To derive the third equation of state we turn to Eq.$(3.11)_{4.2}$. We find

$$\frac{\mu}{T} = -\left.\frac{\partial S}{\partial N}\right|_{U,V} = -\frac{\partial}{\partial N}\left[\frac{NS_0}{N_0} + N\mathrm{f}(U/N) + N\mathrm{R}\,ln\,\frac{VN_0}{V_0N}\right] \qquad (12.2)_5$$

i.e.,

$$\frac{\mu}{T} = -\frac{S_0}{N_0} - \mathrm{f}(U/N) - N\frac{\partial\mathrm{f}(U/N)}{\partial N} - \mathrm{R}\,ln\,\frac{VN_0}{V_0N} + N\mathrm{R}\frac{\partial\,ln\,N}{\partial N}\,, \qquad (12.2)_6$$

so that

$$\frac{\mu}{T} = -\frac{S_0}{N_0} - \mathrm{f}(U/N) + \frac{U}{N}\frac{\partial\mathrm{f}(U/N)}{\partial(U/N)} - \mathrm{R}\,ln\,\frac{VN_0}{V_0N} + \mathrm{R}\,, \qquad (12.2)_7$$

or

$$\frac{\mu}{T} = -s_0 - \mathrm{f}(u) + u/T - \mathrm{R}\,ln\,v/v_0 + \mathrm{R}\,. \qquad (12.2)_8$$

Equation $(12.2)_8$ follows from $(12.2)_7$ because

$$\frac{\partial\mathrm{f}(U/N)}{\partial(U/N)} = \frac{d\mathrm{f}(u)}{du}\,, \qquad (12.2)_9$$

and this equals $1/T$ by Eq.$(12.2)_1$. Equations $(12.2)_7$ and $(12.2)_8$ represent the third equation of state of a single-component ideal gas.

12.3 Equivalence of the Complete Set of the Equations of State with the Fundamental Equation

In § 3.12 we asserted that the complete set of the equations of state is equivalent to the fundamental equation. Indeed, inserting Eqs.$(12.2)_2$, $(12.2)_3$, and $(12.2)_8$ into the molar form of the Euler equation, Eq.$(3.10)_5$, in the entropy representation,

$$s = \frac{1}{T}u + \frac{P}{T}v - \frac{\mu}{T}\,, \qquad (12.3)_1$$

immediately reproduces the fundamental equation, Eq.$(12.1)_1$.

The expectation that substitution of the equations

$$T = u/cR \tag*{(12.3)$_2$}$$

$$P = RT/v \tag*{(12.3)$_3$}$$

and

$$\mu = -s_oT - T\,f(u) + u - RT\,ln v/v_o + RT \tag*{(12.3)$_4$}$$

into the molar form of the Euler equation in the energy representation,

$$u = Ts - Pv + \mu, \tag*{(12.3)$_5$}$$

might lead to the fundamental equation in the energy representation, is not borne out.

In fact, doing so leads to

$$T\,f(u) = us/cR - s_oT - RT\,ln v/v_o \tag*{(12.3)$_6$}$$

and resubstitution of Eq.(12.3)$_2$, multiplication by T, and rearranging leads to

$$f(u) = s - s_oT - RT\,ln v/v_o \tag*{(12.3)$_7$}$$

which we could have obtained simply by solving Eq.(12.2)$_1$ for $f(u)$.

12.4 Empirical Ideal Gas Laws

There are several historical empirical gas 'laws' that are commonly referred to under the name of their originators. Thus the dependence of the internal energy per mole, u, on the temperature only, expressed by the first equation of state in the form $u = cRT$ is sometimes referred to as *Joule's Law*. Several other such laws are seen to follow from the second equation of state. *Boyle's Law* claims that, for a given volume of an ideal gas at the same temperature, $PV = const$, implying that the volume changes inversely as the pressure. The law first enunciated by *Charles* and later independently by *Gay-Lussac* states that at constant pressure a given volume of an ideal gas is directly proportional to the (absolute) temperature. This is expressed by $V = NRT/P$. Finally, *Avogadro's Law* states that at the same temperature and pressure the molar volume of all ideal gases is the same. This follows from $v = V/N = RT/P$.

12.5 The Primary Set of Partial Derivatives for an Ideal Gas

The second equation of state of an ideal gas leads to particularly simple expressions for the primary set of the second-order partial derivatives. Introducing $V = NRT/P$ into Eqs.(10.2)$_2$ and (10.2)$_3$ yields the isobaric expansivity as

$$\alpha_P = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P = \frac{1}{T} \tag*{(12.5)$_1$}$$

and the isothermal compressibility as

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T = \frac{1}{P}\,. \tag{12.5)$_2$ \notag$$

(12.5)$_2$

These two relations apply to any ideal gas, thus also to the monatomic and multicomponent ideal gases to be discussed in detail in Chapters 13 and 15.

The same cannot be said about the isochoric and the isobaric heat capacities of an ideal gas. Differentiation of the entropy, Eq.(12.1)$_2$, with respect to the temperature shows that the heat capacities of an ideal gas are functions of f(u) and, therefore, generally, of the temperature. The monatomic ideal gas is an exception (see § 13). Since f(u) differs from gas to gas for all other ideal gases, so also do $C_V(T)$ and $C_P(T)$. However, combining Eq.(10.3)$_3$, i.e., $c_P = c_V + Tv\alpha_P^2/\kappa_T$, with the equation of state, $Pv = \mathrm{R}T$, gives the *molar heat capacity difference* of any ideal gas as

$$c_P(T) - c_V(T) = \mathrm{R}\,, \qquad (12.5)_3$$

which, for the monatomic ideal gas becomes simply $c_P - c_V = \mathrm{R}$, and for any component of a multicomponent ideal gas takes the form $c_{Pi}(T) - c_{Vi}(T) = \mathrm{R}$ (cf. § 15.4).

12.6 The Fundamental Equations of the Ideal Gas in Parametric Form

Since in an ideal gas u depends on the temperature only, it is possible to express f(u), and thus also the internal energy and the entropy of an ideal gas, in terms of the experimentally accessible molar heat capacities, $c_V(T)$ and $c_P(T)$. In either case the resulting expressions: $s = s(u, v)$ for the entropy, and $u = u(s, v)$ for the internal energy, then constitute two parametric equations for the fundamental equation. The latter could, in principle, be obtained in either the entropy or the energy representation from the parametric equations by elimination of T between them. Because, however, the temperature dependence of the heat capacities is not known explicitly in general, this is possible only in special cases. The *monatomic* ideal gas (cf. § 13.1) represents such a special case

While the parametric equations cannot be combined through the elimination of the temperature into fundamental equations in the energy or the entropy representations, it *is* possible to obtain fundamental equations from the parametric equations in the free energy and in the free enthalpy representations (cf. §§ 12.9 and 12.10). In these cases there is no need for the elimination of the temperature since it is a canonical variable in both these alternative representations.

12.7 The Parametric Fundamental Equations of the Ideal Gas in Terms of $c_V(T)$

We proceed to express the parametric equations of the single-component ideal gas in terms of the temperature dependence of the molar heat capacity at constant volume, $c_V(T)$. This can be determined experimentally and, in some cases, explicit expressions may be obtained from statistical mechanical considerations.

Because u is a function of temperature only, Eq.(10.1)$_4$ becomes

$$du = c_V(T)\,dT\,. \tag{12.7$_1$}$$

and integration yields

$$u = u_o + \int_{T_0}^{T} c_V(T')\,\mathrm{d}T'\,, \tag{12.7$_2$}$$

the molar form of the first of the sought-for parametric equations.

Substituting Eq.(12.7)$_1$ into the first equation of state, $d\mathrm{f}(u) = du/T$, and integrating using $\mathrm{f}(u_o) = 0$, yields

$$\mathrm{f}(u) = \int_{T_0}^{T} \frac{c_V(T')}{T'}\,\mathrm{d}T'\,. \tag{12.7$_3$}$$

Inserting this into Eq.(12.1)$_1$ renders the second parametric equation as

$$s = s_o + \int_{T_0}^{T} \frac{c_V(T')}{T'}\,\mathrm{d}T' + \mathrm{R}\,ln\,v/v_o\,. \tag{12.7$_4$}$$

Equations (12.7)$_2$ and (12.7)$_4$ are the molar parametric equations for a single-component ideal gas in terms of $c_V(T)$, the molar heat capacity at constant volume.

12.8 The Parametric Fundamental Equations of the Ideal Gas in Terms of $c_P(T)$

The last three equations can be rewritten replacing $c_V(T)$ by the experimentally more convenient $c_P(T)$. Using Eq.(12.5)$_3$, i.e., $c_V(T) = c_P(T) - \mathrm{R}$, Eq.(12.6)$_2$ becomes

$$u = u_o + \int_{T_0}^{T} c_P(T')\,\mathrm{d}T' - \mathrm{R}(T - T_o)\,, \tag{12.8$_1$}$$

Eq.(12.7)$_3$ yields

$$\mathrm{f}(u) = \int_{T_0}^{T} \frac{c_P(T')}{T'}\,\mathrm{d}T' - \mathrm{R}\,ln\,T/T_o\,, \tag{12.8$_2$}$$

and Eq.(12.7)$_4$ turns into

$$s = s_o + \int_{T_0}^{T} \frac{c_P(T')}{T'}\, dT' - R\, ln\, T/T_o + R\, ln\, v/v_o \tag{12.8)$_3$}$$

or

$$s = s_o + \int_{T_0}^{T} \frac{c_P(T')}{T'}\, dT' - R\, ln\, P/P_o \tag{12.8)$_4$}$$

where $P_o = RT_o/v_o$. Equations $(12.8)_1$ with $(12.8)_3$ or with $(12.8)_4$ form alternative pairs of the molar parametric equations of the single-component ideal gas in terms of $c_P(T)$, the molar heat capacity at constant pressure.

12.9 The Fundamental Equation of the Ideal Gas in the Free Energy Representation

To derive the expression for the fundamental equation of the ideal gas in the free energy representation, we first multiply the expressions for the molar parametric equations written in terms of the heat capacity at constant volume, $c_V(T)$, by the number of moles, N. This leads to

$$U = N\frac{U_o}{N_o} + N\int_{T_0}^{T} c_V(T')\, dT' \qquad (12.9)_1$$

from Eq.$(12.7)_2$, and to

$$S = N\frac{S_o}{N_o} + N\int_{T_0}^{T} \frac{c_V(T')}{T'}\, dT' + NR\, ln\, v/v_o \qquad (12.9)_2$$

from Eq.$(12.7)_4$. Combining these according to $F = U - TS$ gives

$$F = \frac{N}{N_o}F_o + N\int_{T_0}^{T} \frac{T' - T}{T'}\, c_V(T')\, dT' - NRT\, ln\, v/v_o \qquad (12.9)_3$$

with $F_o = U_o - TS_o$, as the fundamental equation of the ideal gas in the free energy representation.

12.10 The Fundamental Equation of the Ideal Gas in the Free Enthalpy Representation

To obtain the fundamental equation of the ideal gas in the free enthalpy representation we use the parametric equations written in terms of the heat capacity at constant pressure, $c_P(T)$, since we need the pressure as another canonical variable in this case. By multiplying with the number of moles, N, we obtain

$$U = N\frac{U_o}{N_o} + N\int_{T_0}^{T} c_P(T')\,\mathrm{d}T' - N\mathrm{R}(T - T_o) \tag{12.10$_1$}$$

from Eq.(12.8)$_1$, and

$$S = N\frac{S_o}{N_o} + N\int_{T_0}^{T} \frac{c_P(T')}{T'}\,\mathrm{d}T' - N\mathrm{R}\,ln\,P/P_o \tag{12.10$_2$}$$

from Eq.(12.8)$_4$. Using both $G = U - TS + PV$ and $PV = N\mathrm{R}T$ yields

$$G = N\frac{G_o}{N_o} + N\int_{T_0}^{T} \frac{T' - T}{T'}\,c_P(T')\,\mathrm{d}T' + N\mathrm{R}T\,ln\,P/P_o \tag{12.10$_3$}$$

with $G_o = U_o - TS_o + P_oV_o$, as the fundamental equation of the ideal gas in the free enthalpy representation.

12.11 The Gibbs-Duhem Equation of the Ideal Gas in Terms of $c_P(T)$

Multiplication of the third equation of state, Eq.(12.2)$_8$, by T yields

$$\mu = -Ts_o - Tf(u) + u - \mathrm{R}T\,ln\,v/v_o + \mathrm{R}T\,. \tag{12.11$_1$}$$

With the help of Eqs. (12.8)$_1$ and (12.8)$_2$ and the use of $Pv = \mathrm{R}T$ this becomes

$$\mu = \mu_o(T) + \mathrm{R}T\,ln\,P/P_o \tag{12.11$_2$}$$

where

$$\mu_o(T) = u_o - Ts_o + \mathrm{R}T_o + \int_{T_0}^{T} \frac{T' - T}{T'}\,c_P(T')\,\mathrm{d}T'\,. \tag{12.11$_3$}$$

or, alternatively,

$$\mu_o(T) = u_o - Ts_o + \mathrm{R}T - \mathrm{R}T\,ln\,T/T_o) + \int_{T_0}^{T} \frac{T' - T}{T'}\,c_V(T')\,\mathrm{d}T'\,. \tag{12.11$_4$}$$

The function $\mu_o(T)$ is the *standard chemical potential* at the temperature T and the standard (reference) pressure P_o. The zero subscript in $\mu_o(T)$ refers to this pressure. Thus $\mu_o(T)$ is standard with respect to a standard pressure but it is a function of temperature.

Equation (12.11)$_2$ with either (12.11)$_3$ or (12.11)$_4$ provides a functional relation between the intensive parameters T, P, and μ. They thus together represent the integrated form of the Gibbs-Duhem equation of the ideal gas in terms of the molar heat capacities at constant pressure or constant volume. Behavior in accordance with Eq.$(12.11)_2$ constitutes a *sufficient condition* for the ideal behavior of a gas.

13. THE MONATOMIC IDEAL GAS

Among all ideal gases, the *monatomic* ideal gas shows by far the simplest behavior. It is known from statistical mechanics[9] that the constant 'c' in Eq.(12.2)$_2$ has the value 3/2. Thus $c_V = 3\mathrm{R}/2$ by Eqs.(10.1)$_4$ and it follows that $c_P = 5\mathrm{R}/2$. The heat capacities of a monatomic ideal gas thus do not depend on the temperature and this results in considerable simplification of the thermodynamic properties of this gas. In particular, it becomes possible to write an explicit fundamental equation for the monatomic ideal gas, and to obtain this not only in the entropy and energy representation but in the alternative representations as well. In addition, the monatomic ideal gas allows us to demonstrate that, if the equations of state are at hand, the fundamental equation can be obtained through the introduction of the state equations into the Euler equation.

13.0 Chapter Contents

13.1 The Fundamental Equation of the Monatomic Ideal Gas in the Entropy Representation

In the case of a monatomic ideal gas the generally unspecified function $\mathrm{f}(u)$ becomes explicit through the substitution of 3R/2 for $c_V(T)$ in Eq.(12.7)$_3$. Integration yields

$$\mathrm{f}(u) = \frac{3}{2}\mathrm{R}\, lnT/T_o \qquad (13.1)_1$$

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[9] see, e.g., Blinder (1969), p. 274.

and introducing this into Eq.(12.1)$_1$ leads to

$$s = s_o + \frac{3}{2}\,\mathrm{R}\ln T/T_o + \mathrm{R}\,ln\, v/v_o\,. \tag{13.1$_2$}$$

With $c = 3/2$, Eq.(12.2)$_2$ yields $T = 2u/3R$ and we find

$$s = s_o + \frac{3}{2}\,\mathrm{R}\ln u/u_o + \mathrm{R}\,ln\, v/v_o \tag{13.1$_3$}$$

as the molar fundamental equation of the monatomic ideal gas in the entropy representation. Through multiplication by the mole number, N, we obtain

$$S = N\frac{S_o}{N_o} + N\mathrm{R}\,ln\left[\left(\frac{U}{U_o}\right)^{3/2}\frac{V}{V_o}\left(\frac{N}{N_o}\right)^{-5/2}\right] \tag{13.1$_4$}$$

as the fundamental equation in terms of the canonical variables U, V, and N.

We note that this derivation is tantamount to an elimination of T between the parametric equations that play a prominent role in Chapters 12 and 15.

13.2 The Fundamental Equation of the Monatomic Ideal Gas in the Energy Representation

Equation (13.1)$_3$ can be solved for $u = u(s, v)$ to yield the molar fundamental equation of the monatomic ideal gas in the internal energy representation as

$$u = u_o(v_o/v)^{2/3}\exp[(2/3\mathrm{R})(\mathrm{s} - \mathrm{s_o})]\,. \tag{13.2$_1$}$$

We recall that we were not able to obtain $u = u(s, v)$ for the general ideal gas (cf. § 12.3).

Multiplication by the mole number, N, gives the fundamental equation of the monatomic ideal gas in the internal energy representation as

$$U = N\frac{U_o}{N_o}\left(\frac{V_oN}{VN_o}\right)^{2/3}\exp\left[\frac{2}{3\mathrm{R}}\left(\frac{S}{N} - \frac{S_o}{N_o}\right)\right] \tag{13.2$_2$}$$

in terms of the canonical variables S, V, and N.

13.3 The Fundamental Equation of the Monatomic Ideal Gas in the Enthalpy Representation

By Eq.(8.13)$_1$ the enthalpy, H, is given by

$$H = U + PV\,. \tag{13.3$_1$}$$

To obtain H for the monatomic ideal gas in term of the canonical variables, S, P, and N, we first need to solve Eq.$(13.1)_4$ for V. This gives

$$V = V_o\left(\frac{N}{N_o}\right)\left(\frac{P_o}{P}\right)^{3/2}\exp\left[\frac{2}{5R}\left(\frac{S}{N} - \frac{S_o}{N_o}\right)\right]. \qquad (13.3)_2$$

Combining Eqs.$(13.2)_2$ and $(13.3)_2$ according to Eq. $(13.3)_1$ leads to

$$H = H_o\left(\frac{N}{N_o}\right)\left(\frac{P}{P_o}\right)^{2/5}\exp\left[\frac{2}{5R}\left(\frac{S}{N} - \frac{S_o}{N_o}\right)\right] \qquad (13.3)_3$$

where $H_o = \frac{5}{2}P_oV_o$.

Equation $(13.3)_3$ is the fundamental equation of the monatomic ideal gas in the enthalpy representation in terms of the canonical variables S, P, and N. The molar form follows as

$$h = h_o(P/P_o)^{2/5}\exp[(2/3R)(s - s_o)]\,. \qquad (13.3)_4$$

where $h_o = 5P_ov_o/2$.

13.4 The Fundamental Equation of the Monatomic Ideal Gas in the Free Energy Representation

The free energy, F, is given by Eq.$(8.10)_1$ as

$$F = U - TS\,. \qquad (13.4)_1$$

Combining Eqs.$(13.2)_2$ and $(13.1)_4$ according to Eq.$(13.4)_1$ we obtain

$$F = F_o\frac{NT}{N_oT_o} - NRT\,ln\left[\left(\frac{T}{T_o}\right)^{3/2}\frac{VN_o}{V_oN}\right], \qquad (13.4)_2$$

where $F_o = U_o - T_oS_o$.

Equation $(13.4)_2$ is the fundamental equation of the monatomic ideal gas in the free energy representation in terms of the canonical variables T, V, and N. Its molar form is

$$f = f_oT/T_o - RT\,ln\left[\left(T/T_o\right)^{3/2}v/v_o\right] \qquad (13.4)_3$$

where $f_o = u_o - Ts_o$.

13.5 The Fundamental Equation of the Monatomic Ideal Gas in the Free Enthalpy Representation

Equation $(8.16)_1$ gives the free enthalpy as

$$G = H - TS. \tag{13.5)$_1$}$$

Combining Eqs.$(13.3)_3$ and $(13.1)_4$ according to Eq.$(13.5)_1$ leads to

$$G = G_o \frac{NT}{N_o T_o} - N\mathrm{R}T\, ln\left[\left(\frac{T}{T_o}\right)^{5/2} \frac{P}{P_o}\right], \qquad (13.5)_2$$

where $G_o = U_o - T_o S_o + P_o V_o$.

Equation $(13.5)_2$ is the fundamental equation of the monatomic ideal gas in the free enthalpy representation in terms of the canonical variables T, P, and N. The molar form becomes

$$g = g_o T/T_o - \mathrm{R}T\, ln\left[\left(T/T_o\right)^{5/2} P/P_o\right], \qquad (13.5)_3$$

where $g_o = u_o - Ts_o + P_o v_o$.

13.6 The Equations of State of the Monatomic Ideal Gas in the Entropy Representation

The equations of state of the monatomic ideal gas in the entropy representation follow at once from Eq.$(13.1)_4$ as

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N} = \frac{3N\mathrm{R}}{2U} = \frac{3\mathrm{R}}{2u}, \qquad (13.6)_1$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} = \frac{N\mathrm{R}}{V} = \frac{\mathrm{R}}{v}, \qquad (13.6)_2$$

and

$$\begin{aligned} \frac{\mu}{T} = -\left.\frac{\partial S}{\partial N}\right|_{U,V} &= \frac{5}{2}\mathrm{R} - \frac{S_o}{N_o} - \frac{3}{2}\mathrm{R}\, ln\frac{UN_o}{U_oN} - \mathrm{R}\, ln\frac{VN_o}{V_oN} \\ &= 2.5\,\mathrm{R} - s_o - 1.5\,\mathrm{R}\, ln\, u/u_o - \mathrm{R}\, ln\, v/v_o \end{aligned} \qquad (13.6)_3$$

where we have given the molar forms also.

13.7 The Equations of State of the Monatomic Ideal Gas in the Energy Representation

Since we now have an explicit fundamental equation in the energy representation, we may obtain the equations of state in that representation also. Applying Eq.$(3.11)_1$ we get

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N} = \frac{2}{3\mathrm{R}}\frac{U_o}{N_o}\left(\frac{V_oN}{VN_o}\right)^{2/3} \exp\left[\frac{2}{3\mathrm{R}}\left(\frac{S}{N} - \frac{S_o}{N_o}\right)\right] \qquad (13.7)_1$$

$$P = -\left.\frac{\partial U}{\partial V}\right|_{S,N} = \left(\frac{2}{3}\frac{N}{V}\right)\frac{U_o}{N_o}\left(\frac{V_oN}{VN_o}\right)^{2/3} \exp\left[\frac{2}{3\mathrm{R}}\left(\frac{S}{N} - \frac{S_o}{N_o}\right)\right] \qquad (13.7)_2$$

and

$$\mu = \left.\frac{\partial U}{\partial N}\right|_{S,V} = \left(1 - \frac{2}{3\mathrm{R}}\frac{S}{N}\right)\frac{U_o}{N_o}\left(\frac{V_oN}{VN_o}\right)^{2/3} \exp\left[\frac{2}{3\mathrm{R}}\left(\frac{S}{N} - \frac{S_o}{N_o}\right)\right] \qquad (13.7)_3$$

We make use of these equations of state in the next section.

13.8 Equivalence of the Complete Set of the Equations of State with the Fundamental Equation – Revisited

In § 12.3 we demonstrated that the complete set of equations of state of the general ideal gas is equivalent to the fundamental equation in the entropy representation. This is, of course, also true of the monatomic gas. Substituting Eqs.$(13.6)_1$ to $(13.6)_3$ into the Euler equation,

$$S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}N, \qquad (13.8)_1$$

we promptly recover Eq.$(13.1)_4$.

In the case of the general ideal gas we were not able to obtain the fundamental equation in the energy representation from the equations of state (cf. § 12.3). Now, however, substitution of Eqs.$(13.7)_1$ to $(13.7)_3$ into the Euler equation,

$$U = TS - PV + \mu N, \qquad (13.8)_1$$

in the energy representation leads, after some algebra, to the fundamental equation, Eq.$(13.2)_2$, as expected.

13.9 The Domain of Validity of the Fundamental Equation of the Monatomic Ideal Gas

By Postulate V, Eq.(2.21), the partial derivative of the internal energy with respect to the entropy, Eq.$(13.7)_1$, when equated to zero, should yield the entropy, S, as a positive semi-definite quantity. However, $\partial U/\partial S = 0$ requires that $S = -\infty$. The fundamental equation for the monatomic ideal gas thus violates Postulate V.

The reason, of course, is that the equations of state derived in § 13.7 are approximations to the *true* equations of state and these approximations are valid only under the assumptions of high temperatures $(T \to \infty)$ and low pressures $(P \to 0)$. The assumptions are implicit also in the quantum mechanical derivation of the fundamental equation (see Appendix 4). Even in the case of the monatomic ideal gas, the *true* fundamental equation thus remains unknown. Equation $(13.1)_4$ is therefore valid only at sensibly high temperatures and low pressures, and these conditions define its *domain of validity* The fact that the fundamental equation (and the equations of state) are valid only over a range of the intensive parameters does not impair their utility as long as they are applied within their domain of validity

13.10 The Gibbs-Duhem Equation for the Monatomic Ideal Gas

The Gibbs-Duhem equation for the monatomic ideal gas is identical with Eqs.$(12.11)_2$ or $(12.12)_1$ for the general ideal gas,

$$\mu = \mu_o(T) + RT\, ln\, P/P_o\,, \tag*{$(13.10)_1$}$$

except that the standard chemical potential, $\mu_o(T)$, now simplifies to

$$\mu_o(T) = u_o - Ts_o - \frac{3}{2}RT_o + \frac{5}{2}RT(1 - ln\, T/T_o) \tag*{$(13.10)_2$}$$

either through substitution of $c_P(T)$ into Eq.$(12.11)_3$, or of $c_V(T)$ into Eq.$(12.12)_2$.

Equations $(13.10)_1$ and $(13.10)_2$ together represent the integrated form of the Gibbs-Duhem equation of a monatomic ideal gas. Conformance with Eq.$(13.10)_1$ constitutes a *sufficient condition* for the ideal behavior of a monatomic gas just as it does for the ideal behavior of a general gas.

14. THE IDEAL MIXTURE

Most thermodynamic systems consist of more than one component. Macroscopically homogeneous multicomponent systems form *mixtures*. By contrast, *blends* are multicomponent systems that are not homogeneous. Mixtures may be gases or condensed systems (liquids or solids). We will be concerned primarily with the ideal gas mixture (the multicomponent ideal gas, Chapter 15) and with the ideal solution (Chapter 16).

A discussion of the thermodynamics of mixtures requires the concepts of molar and partial molar quantities, and of mole fractions. These concepts, together with a discussion of those characteristics of the ideal mixture that are common to the multicomponent ideal gas and the ideal solution, form the topic of the present chapter. We will use the terms *mixture* and *multicomponent system* interchangeably.

The simplest mixture is the two-component mixture or *binary system*. It will receive special attention wherever called for.

14.0 Chapter Contents

14.1 Molar Quantities

In a single-component system with constant composition, division of any of the extensive parameters by the mole number, N, yields the corresponding *molar* quantity. We shall denote this by the corresponding lower case letter. Thus,

- $U/N = u$ is the internal energy per mole or *molar internal energy*,
- $S/N = s$ is the entropy per mole or *molar entropy*,
- $V/N = v$ is the volume per mole or *molar volume*, etc.

The molar quantities are intensive parameters. Some molar quantities had already been used earlier.

14.2 The Molar Fundamental Equation

As an example of the use of molar quantities we express the fundamental equation, of a single-component simple system, in terms of the molar quantities. Since the fundamental equation is homogeneous of the first order in its canonical variables (cf. § 3.1), we have

$$S(U,V,N) = NS(U/N,V/N,1) \qquad (14.2)_1$$

or

$$S(U,V,N)/N = S(u,v,1)\,. \qquad (14.2)_2$$

Thus we have

$$s = s(u,v) \qquad \text{and} \qquad u = u(s,v) \qquad (14.2)_3$$

for the *molar fundamental equation* of the single-component simple system in the entropy and in the energy representations.

Molar forms of the fundamental equations have, of course, been used already in the preceding chapters.

14.3 The Molar Gibbs and Euler Equations

Both the Gibbs and the Euler equations also have molar forms. In the energy representation the *molar Gibbs equation* for the single-component simple system becomes

$$du = Tds - Pdv\,, \qquad (14.3)_1$$

and the Euler equation takes the form

$$u = Ts - Pv + \mu\,. \qquad (14.3)_2$$

In the entropy representation we have

$$ds = \frac{1}{T}du + \frac{P}{T}dv \qquad (14.3)_3$$

and

$$s = \frac{1}{T}u + \frac{P}{T}v \qquad (14.3)_4$$

for both equations.

14.4 Partial Molar Quantities

In a multicomponent simple system we require a set of thermodynamic quantities which represent the contributions of the ith component to each extensive variable of the system. These quantities are the *partial* molar quantities. Just like the molar ones, the partial molar quantities are intensive parameters They are defined as follows.

Let X be an extensive property of the ith component. Then

$$\left.\frac{\partial X}{\partial N_i}\right|_{T,P,\ldots N_{j(\neq i)}\ldots} = \overline{X}_i \qquad (14.4)_1$$

where the overbar indicates the partial molar value of the property X for the ith component. As an example, in a binary solution, $\overline{V}_1$ would be the partial molar volume of the solvent, and $\overline{V}_2$ would be the partial molar volume of the solute. We note that the partial molar values of those extensive properties that are not measurable directly (U, S) must, of course, be calculated with respect to the same reference state as the extensive property itself.

Since X is extensive, hence additive, we have

$$X = \sum\nolimits_i N_i \overline{X}_i\,. \qquad (14.4)_2$$

For a pure substance

$$\overline{X}_i = x_i, \qquad (14.4)_3$$

i.e., the partial molar quantities of a pure substance are identical with the molar quantities.

14.5 Mole Fractions

The quantity

$$\overline{n}_i \;=\; N_i/N \qquad (14.5)_1$$

where $N = \Sigma_i N_i$, is called the *mole fraction of component i*. By definition,

$$\sum\nolimits_i \overline{n}_i = 1\,, \qquad (14.5)_2$$

i.e., the sum of the mole fractions is unity.

14.6 Partial Molar Quantities and the Chemical Potential

Rewriting Eq.(8.16)$_4$ for a single component we see that at constant temperature and pressure the chemical potential of a single component simple system is

$$\mu = \left.\frac{\partial G}{\partial N}\right|_{T,\,P} . \tag{14.6$_1$}$$

It is thus equal to the molar free enthalpy, g, since, be Eq.(8.16)$_6$,

$$\left.\frac{\partial G}{\partial N}\right|_{T,\,P} = G/N = g \tag{14.6$_2$}$$

for a single-component simple system.

In a multicomponent simple system (i.e., a mixture) the partial derivatives with respect to the mole number, N, are replaced by the partial molar quantities. The chemical potential of the ith component thus becomes

$$\mu_i = \left.\frac{\partial G}{\partial N_i}\right|_{T,\,P,\,\overline{N}} \tag{14.6$_3$}$$

where, for convenience, we have written $\overline{N}$ for $\ldots N_j(\neq N_i)\ldots$. We now have

$$\left.\frac{\partial G}{\partial N_i}\right|_{T,\,P,\ldots N_{j(\neq i)}\ldots} = \overline{G}_i = \mu_i . \tag{14.6$_4$}$$

i.e., the chemical potential of the ith component of a multicomponent simple system is the partial molar free enthalpy of that component.

14.7 Dependence of the Chemical Potential on Composition

In accordance with Eq.(11.3)$_2$ at constant temperature and pressure the chemical potential of the ith component of an ideal mixture depends only on the mole fractions, $\overline{n}_i$. This dependence is given by the notably simple relation

$$\mu_i = \mu_i(T,\,P,\,\overline{n}_i) = \mu_i^*(T,\,P) + RT\;ln\,\overline{n}_i \tag{14.7}$$

where $\mu_i^*(T,\,P)$ is the value of μ_i when $\overline{n}_i = 1$. It is thus the chemical potential of the ith *pure substance* at the temperature and pressure of the mixture. Behavior in accordance with Eq.(14.7) constitutes a *sufficient condition* for the ideal behavior of a multicomponent simple system or mixture.

14.8 Change in the Chemical Potential upon Mixing

By Eqs.(14.6)$_1$ and (14.6)$_2$, the change in the chemical potential of the ith component upon mixing at constant temperature and pressure is

$$\Delta\mu_i = \left.\frac{\partial \Delta G}{\partial N_i}\right|_{T,\,P,\ldots N_j\,(\neq N_i)\ldots} . \tag{14.8}$$

For an ideal gas mixture Eqs.(14.6)$_4$ and (14.8) apply without reservation. Provided the molecular structure of the components is closely similar they also apply to condensed systems (liquids and solids). A mixture of isotopes constitutes a case in point.

14.9 Changes in Volume upon Mixing

The mixing of ideal components into an ideal mixture does not produce any changes in either volume, enthalpy, or internal energy. To show this, we proceed as follows.

Partial differentiation of Eq.(14.7) with respect to P yields

$$\left.\frac{\partial \mu_i}{\partial P}\right|_{T,\ldots \bar{n}_i\ldots} = \left.\frac{\partial \mu_i^*(T,P)}{\partial P}\right|_T . \tag{14.9)$_1$$$

The right-hand-side is independent of composition and thus so is the left. But, by the third of the Maxwell relations, Eqs.(10.6)$_4$,

$$\left.\frac{\partial \mu_i}{\partial P}\right|_{T,\ \ldots N_{m(\neq i)}\ldots} = \left.\frac{\partial V}{\partial N_i}\right|_{T,\,P,\ldots N_{m(\neq i)}\ \ldots} = \overline{V}_i = v_i\,. \qquad (14.9)_2$$

The last relation follows from Eq.(14.4)$_3$. An ideal mixture thus exhibits no volume change upon mixing and thus

$$\Delta V_{\text{mix}} = 0\,. \qquad (14.9)_3$$

because $V = \sum_i N_i \overline{V}_i = \sum_i N_i v_i$.

14.10 Changes in Enthalpy upon Mixing

Dividing Eq.(14.7) by T and then differentiating with respect to T yields

$$\left.\frac{\partial \mu_i/T}{\partial T}\right|_{P,\ \ldots N_{m(\neq i)}\ldots} = \left.\frac{\partial \mu_i^*(T,P)/T}{\partial T}\right|_P . \qquad (14.10)_1$$

Since the right-hand-side of this equation is independent of composition, so is the left. By the second of the Maxwell relations, Eqs.(10.6)$_4$,

$$\left.\frac{\partial \mu_i}{\partial T}\right|_{P,\ \ldots N_{m(\neq i)}\ldots} = -\left.\frac{\partial S}{\partial N_i}\right|_{T,P,\ldots N_{m(\neq i)}\ \ldots} = \overline{S}_i\,. \tag{14.10$_2$}$$

But, by Eq.(14.6)$_4$,

$$\mu_i = \overline{G}_i = \overline{H}_i - T\overline{S}_i\,. \tag{14.10$_3$}$$

where $\overline{H}_i$ and $\overline{S}_i$ are the partial molar enthalpy, and entropy, respectively. Combining these two equations, and rearranging, gives

$$\left.\frac{\partial \mu_i/T}{\partial T}\right|_{P,\ \ldots N_{m(\neq i)}\ldots} = -\frac{\overline{H}_i}{T^2} = -\frac{h_i}{T^2}\,. \tag{14.10$_4$}$$

Again, the last relation follows since $H = \sum_i N_i\overline{H}_i = \sum_i N_i h_i$. Hence, the total enthalpy of the mixture is equal to the sum of the enthalpies of the components before mixing and thus

$$\Delta H_{\text{mix}} = 0\,. \tag{14.10$_5$}$$

i.e., the heat of mixing is zero.

14.11 Changes in Internal Energy upon Mixing

Because $\Delta U_{\text{mix}} = \Delta H_{\text{mix}} - P\Delta V_{\text{mix}}$ it follows immediately that

$$\Delta U_{\text{mix}} = 0\,, \tag{14.11}$$

i.e., that the internal energy of mixing is also zero.

14.12 The Free Enthalpy, Free Energy, and Entropy of Mixing of an Ideal Mixture

Similar relations do not hold for the free enthalpy of mixing, ΔG_{mix}, the free energy of mixing, ΔF_{mix}, and the entropy of mixing, ΔS_{mix}. For mixing to occur, the change in the free enthalpy of the mixture, i.e., the difference between the free enthalpy before and after mixing, must be negative. Since mixing is an irreversible process (you cannot unscramble eggs, as Bertrand Russell put it), the change in entropy, i.e., the entropy of mixing, ΔS_{mix}, is necessarily positive. Hence, the free enthalpy of mixing becomes

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = -T\Delta S_{\text{mix}} \tag{14.12$_1$}$$

since $\Delta H_{\text{mix}} = 0$ by Eq.(14.10)$_5$.

In an analogous way the free energy of mixing, ΔF_{mix}, in an ideal mixture is given by

$$\Delta F_{\text{mix}} = \Delta U_{\text{mix}} - T\Delta S_{\text{mix}} = -T\Delta S_{\text{mix}}. \qquad (14.12)_2$$

Because of the absence of heat effects upon mixing, in an ideal mixture ΔG_{mix}, ΔF_{mix}, and ΔS_{mix}, are called the *athermal* free enthalpy, the *athermal* free energy, and the *athermal* entropy of mixing.

14.13 General Comments on Changes in the Thermodynamic Potentials upon Mixing

To be valid, the relations $\Delta V_{\text{mix}} = 0$, $\Delta H_{\text{mix}} = 0$, and $\Delta U_{\text{mix}} = 0$ require that all components be at the same temperature. With this proviso they apply equally to the multicomponent ideal gas (Chapter 15), and to the ideal solution (Chapter 16).

Explicit expressions for ΔG_{mix} and ΔS_{mix} will be given for the multicomponent ideal gas in § 15.13. For the ideal solution the expression for ΔS_{mix} will be found in § 16.7, and that for the free enthalpy of dilution, $\Delta\overline{G}_1$, in §16.8.

14.14 The Gibbs-Duhem Equation of a Mixture – The Binary Mixture

By Eq.(8.22)$_5$, at constant temperature and pressure, the Gibbs-Duhem equation of a multicomponent simple system or mixture becomes

$$\sum\nolimits_m N_m\, d\mu_m = 0\,. \qquad (T, P = const) \qquad (14.14)_1$$

Clearly, the chemical potentials are not independent of each other and one can always be expressed in terms of the others.

The simplest—and most frequently encountered—multicomponent simple system is the *two-component simple system,* or *binary system* or *mixture*. Let 1 and 2 denote the two components of a binary mixture. Its Gibbs-Duhem equation at constant temperature and pressure becomes

$$N_1 d\mu_1 + N_2 d\mu_2 = 0 \qquad (T, P = const) \qquad (14.14)_2$$

and can be brought into a form that relates the two chemical potentials to each other.

The binary system is characterized by a single mole fraction since $\overline{n}_1 + \overline{n}_2 = 1$. Letting Z stand for either 1 or 2, the infinitesimal variation of μ_Z in terms of T, P, and $\overline{n}_1$ becomes

$$d\mu_Z = \frac{\partial \mu_Z}{\partial T} dT + \frac{\partial \mu_Z}{\partial P} dP + \frac{\partial \mu_1}{\partial \overline{n}_1} d\overline{n}_1\,. \qquad (14.14)_3$$

Equating the second-order mixed partial derivatives of

$$dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2 \tag{14.14$_4$}$$

with respect to T and N_1, and to P and N_1, respectively, we recognize that

$$\frac{\partial \mu_Z}{\partial T} = -\frac{\partial S}{\partial N_Z} = -\overline{S}_Z \tag{14.14$_5$}$$

and

$$\frac{\partial \mu_Z}{\partial P} = \frac{\partial V}{\partial N_Z} = \overline{V}_Z\,. \tag{14.14$_6$}$$

Hence, Eq.(14.14)$_3$ becomes

$$d\mu_Z = -\overline{S}_Z dT + \overline{V}_Z dP + \frac{\partial \mu_Z}{\partial \overline{n}_1} d\overline{n}_1 \tag{14.14$_7$}$$

Inserting $d\mu_1$and $d\mu_2$ from $d\mu_Z$ into Eq.(14.14)$_2$, canceling terms, and dividing by $N = N_1 + N_2$ yields

$$\overline{n}_1 \left.\frac{\partial \mu_1}{\partial \overline{n}_1}\right|_{T,P} + (1-\overline{n}_1)\left.\frac{\partial \mu_2}{\partial \overline{n}_1}\right|_{T,P} = 0 \tag{14.14$_8$}$$

or, using $\overline{n}_1 = 1 - \overline{n}_2$,

$$\overline{n}_1 \left.\frac{\partial \mu_1}{\partial \overline{n}_1}\right|_{T,P} = \overline{n}_2 \left.\frac{\partial \mu_2}{\partial \overline{n}_2}\right|_{T,P} \tag{14.14$_9$}$$

as two forms of the Gibbs-Duhem equation for a binary system that relate the two chemical potentials, μ_1 and μ_2, to one another at constant temperature and pressure.

15. THE MULTICOMPONENT IDEAL GAS

A multicomponent gas is a mixture of gases. This chapter discusses the properties of a simple multicomponent gas whose extensive variables are U, S, V, and $N_1, \ldots N_i \ldots$. The relations derived in Chapter 12 for a single-component ideal gas with the extensive variables U, S, V, and N, remain substantially the same for a multicomponent ideal gas. However, the internal energy and the entropy of the multicomponent gas are the sums of the internal energies and the entropies of the component gases, and the total number of moles is the sum of the number of moles of the components. We have $U = \Sigma_i U_i$, $S = \Sigma_i S_i$, and $N = \Sigma_i N_i$. Thus, the expressions for the multicomponent ideal gas are obtained simply by summing over the expressions for all components. These, in turn, are obtained by considering the expressions for the single-component gas to be those for the ith component, and labeling them accordingly.

15.0 Chapter Contents

15.1 The Fundamental Equation of the Multicomponent Ideal Gas in the Entropy Representation

We obtain the molar fundamental equation of the ith component of the multicomponent ideal gas in the entropy representation by rewriting the equation of the general ideal gas, Eq.$(12.1)_1$, for the ith component multicomponent ideal gas. Thus, we write

$$s_i = s_{oi} + \mathrm{f}(u_i) + \mathrm{R}\, ln\, v/v_o\,. \tag{15.1}$$

the molar fundamental equation of the ith component multicomponent ideal gas

15.2 The Molar Internal Energy and Molar Entropy of a Multicomponent Ideal Gas

It follows from $U = \Sigma_i U_i$, $S = \Sigma_i S_i$, and $N = \Sigma_i N_i$ that the molar internal energy and molar entropy of a multicomponent ideal gas become

$$u = \frac{U}{N} = \sum\nolimits_i \frac{N_i}{N}\frac{U_i}{N_i} = \sum\nolimits_i \overline{n}_i u_i \tag{15.2$_1$}$$

and

$$s = \frac{S}{N} = \sum\nolimits_i \frac{N_i}{N}\frac{S_i}{N_i} = \sum\nolimits_i \overline{n}_i s_i \tag{15.2$_2$}$$

where $\overline{n}_i$ is the mole fraction, $u_i = U_i/N_i$ is the molar internal energy, and $s_i = S_i/N_i$ is the molar entropy of the ith component. The last two equations allow us to obtain the fundamental equation of the multicomponent ideal gas in parametric form.

15.3 The Equations of State of the Multicomponent Ideal Gas

The equations of state of the multicomponent ideal gas are obtained from the fundamental equation in the usual way by taking the appropriate derivatives. For the first equation this simply confirms that the internal energy of each component, u_i, is still a function of T only, and so, therefore, is the total internal energy, U. For the second equation we recover Eq.(12.2)$_4$, i.e., $PV = N\mathrm{R}T$, where now N is the total number of moles of all components.

The third equation of state of the single-component ideal gas, Eq.(12.2)$_8$, is valid for each component of the multicomponent gas. We thus have $i = 1, 2, \ldots$ equations of the form

$$\frac{\mu_i}{T} = -\,\mathrm{s}_{0i} - \mathrm{f}(u_i) + \frac{u_i}{T} - \mathrm{R}\,ln\, v/v_0 + \mathrm{R}\,. \tag{15.3}$$

Equations (15.3) may be made explicit through introduction of the molar heat capacities at constant volume or at constant pressure by using either Eqs.(12.7)$_2$ and (12.7)$_3$, or Eqs.(12.8)$_1$ and (12.8)$_2$, writing them for $\mathrm{f}(u_i)$ and u_i.

15.4 The Primary Set of Partial Derivatives for a Multicomponent Ideal Gas

Since the ideal gas equation of state, $PV = N\mathrm{R}T$, applies to the multicomponent as well as to the single-component ideal gas, Eqs.(12.5)$_1$ for the isobaric expansivity and (12.5)$_2$ for the isothermal compressibility are equally valid for a multicomponent ideal gas. Equation (12.5)$_3$ for the molar heat capacity difference is then simply rewritten as

$$c_{Pi}(T) - c_{Vi}(T) = \mathrm{R} \tag{15.4}$$

for each of the components.

15.5 The Parametric Equations of the Multicomponent Ideal Gas in Terms of $c_V(T)$

As we have done in the case of the general ideal gas, we express the fundamental equation of the multicomponent ideal gas in parametric form making use of the heat capacities at constant volume, and at constant pressure, respectively.

In terms of the molar heat capacity at constant volume we obtain the parametric equations of the ith components from Eqs.(12.7)$_2$ and (12.7)$_4$ as

$$u_i = u_{oi} + \int_{T_o}^{T} c_{Vi}(T')\,dT' \tag{15.5)$_1$}$$

and

$$s_i = s_{oi} + \int_{T_o}^{T} \frac{c_{Vi}(T')}{T'}\,dT' + \mathrm{R}\,ln\,v/v_o - \mathrm{R}\,ln\,\overline{n}_i \tag{15.5)$_2$}$$

The reference molar internal energy, u_{oi}, and molar entropy, s_{oi}, differ from gas to gas. The other reference quantities, V_o, N_o, T_o, and $v_o = V_o/N_o$, are the same for all components.

Summing over all components according to Eqs.(15.5)$_1$ and (15.2)$_2$ yields

$$u = \sum\nolimits_i \overline{n}_i u_{oi} + \sum\nolimits_i \overline{n}_i \int_{T_o}^{T} c_{Vi}(T')\,dT' \tag{15.5)$_3$}$$

and

$$s = \sum\nolimits_i \overline{n}_i s_{oi} + \sum\nolimits_i \overline{n}_i \int_{T_o}^{T} \frac{c_{Vi}(T')}{T'}\,dT' + N\mathrm{R}\,ln\,v/v_o - \mathrm{R}\sum\nolimits_i \overline{n}_i\,ln\,\overline{n}_i \tag{15.5)$_4$}$$

as the parametric equations of the fundamental equation of the multicomponent ideal gas in terms of the molar heat capacities at constant volume.

15.6 The Parametric Equations of the Multicomponent Ideal Gas in Terms of $c_P(T)$

In terms of the molar heat capacity at constant pressure an analogous derivation yields

$$u_i = u_{oi} + \int_{T_o}^{T} c_{Pi}(T')\,dT' - \mathrm{R}(T - T_o) \tag{15.6)$_1$}$$

and

$$s_i = s_{oi} + \int_{T_o}^{T} \frac{c_{Pi}(T')}{T'}\,dT' - \mathrm{R}\,ln\,P/P_o - \mathrm{R}\,ln\,\overline{n}_i\,. \tag{15.6)$_2$}$$

Summing over all components then yields

$$u = \sum\nolimits_i \bar{n}_i u_{oi} + \sum\nolimits_i \bar{n}_i \int_{T_o}^{T} c_{Pi}(T')\,dT' \; - N\mathrm{R}(T - T_o)\,. \qquad (15.6)_3$$

and

$$s = \sum\nolimits_i \bar{n}_i s_{oi} + \sum\nolimits_i \bar{n}_i \int_{T_o}^{T} \frac{c_{Pi}(T')}{T'}\,dT' - \mathrm{R}\,ln\,P/P_o - \mathrm{R}\sum\nolimits_i \bar{n}_i\,ln\,\bar{n}_i\,. \qquad (15.6)_4$$

In Eqs.$(15.6)_2$ and $(15.6)_4$ the reference pressure, $P_o = \mathrm{R}T_o v_o$, is the same for all components.

15.7 The Extended Gibbs Theorems

The contents of Eqs.$(15.5)_3$ and $(15.6)_3$, and of Eq.$(15.5)_4$ can be expressed in two statements known as the *Gibbs theorems*. These are:

> *"The internal energy of a multicomponent ideal gas is equal to the sum of the energies that each gas would have at the same temperature."*

and

> *"The entropy of a multicomponent ideal gas is equal to the sum of the entropies that each gas would have if it alone occupied the same volume at the same temperature."*

These statements may be extended by adding another embodying the content of Eq.$(15.6)_4$:

> *"The entropy of a multicomponent ideal gas is equal to the sum of the entropies that each gas would have if it alone were at the same pressure and the same temperature."*

15.8 Dalton's Law

Dalton's law expresses a fundamental property of a mixture of ideal gases. It says:

> *"The pressure of a mixture of gases is equal to the sum of the pressures that each of its components would exert if it alone were to occupy the volume at the same temperature".*

In symbols Dalton's law becomes

$$P = \sum\nolimits_i P_i \qquad (15.8)_1$$

where

$$P_i = P\bar{n}_i \qquad (15.8)_2$$

is the *partial pressure* of the ith component. The partial pressure is defined as the pressure the ith component would exert if it alone were present in the volume of the mixture at the same temperature. The sum of all partial pressure is equal to the total pressure, P. A mixture of gases obeying Dalton's Law is an *ideal mixture of gases* even if its components are not.

15.9 Amagat's Law

Amagat's law mirrors, as it were, Dalton's. It has reference to volumes instead of pressures, and claims that

> *"The volume of a mixture of gases is the sum of the volumes of its components, each at the pressure and temperature of the mixture".*

In terms of the partial molar volumes Amagat's Law becomes simply

$$V = \sum_i N_i \overline{V}_i \tag{15.9}$$

[cf. Eq.(14.4)$_2$].

15.10 The Fundamental Equations of the Multicomponent Ideal Gas in the Free Energy Representation

In §§ 12.9 and 12.10 we introduced the fundamental equations of the single-component ideal gas in the free energy and the free enthalpy representation. We now do the same for the ith components of the multicomponent ideal gas. Combining Eqs.(15.5)$_1$ and (15.5)$_2$ according to $f_i = u_i - Ts_i$ furnishes

$$f_i = f_{oi} + \int_{T_o}^{T} \frac{T' - T}{T'} \, c_{Vi}(T')\, dT' - RT \ln v/v_o \qquad (15.10)_1$$

with $f_{oi} = u_{oi} - Ts_{oi}$ as the ith component of the free energy of the multicomponent ideal gas.

Summing over all components we obtain

$$f = \sum_i \overline{n}_i f_{oi} + \sum_i \overline{n}_i \int_{T_o}^{T} \frac{T' - T}{T'} \, c_{Vi}(T')\, dT' - NRT \ln v/v_o\,. \qquad (15.10)_2$$

as the molar free energy of the multicomponent ideal gas.

15.11 The Fundamental Equations of the Multicomponent Ideal Gas in the Free Enthalpy Representation

Analogously, combination of Eqs.(15.6)$_1$ and (15.6)$_2$ using $g = u_i - Ts_i + P_i$ and $P_i v = RT$ yields

$$g_i = g_{oi} + \int_{T_o}^{T} \frac{T' - T}{T'} c_{Pi}(T')\, dT' + RT\, ln\, P_i/P_o \qquad (15.11)_1$$

with $g_{oi} = u_{oi} - Ts_{oi} + P_i v_o$ as the *i*th component of the free enthalpy of the multicomponent ideal gas.

Summing over all components yields

$$g = \sum_i \overline{n}_i g_{oi} + \sum_i \overline{n}_i \int_{T_o}^{T} \frac{T' - T}{T'} c_{Pi}(T')\, dT' + NRT\, ln\, P/P_o \qquad (15.11)_2$$

as the molar free enthalpy of the ideal multicomponent gas.

15.12 The Gibbs-Duhem Equations of a Multicomponent Ideal Gas

To obtain the integrated form of the Gibbs-Duhem equation for the *i*th component of a multicomponent ideal gas we rewrite Eq.$(12.11)_1$ as

$$\mu_i = \mu_{oi}(T) + RT\, ln\, P_i/P_o \qquad (15.12)_1$$

where P_i is the partial pressure (cf. § $15.8)_2$ of the *i*th component. Using $P_i = P\overline{n}_i$, μ_i becomes

$$\mu_i = \mu_{oi}(T) + RT\, ln\, P/P_o + RT\, ln\, \overline{n}_i\, . \qquad (15.12)_2$$

Thus, at constant temperature and pressure, the chemical potential, μ_i, of component i depends only on its own mole fraction, $\overline{n}_i$, and not on the mole fraction of any other component. We remark that letting

$$\mu_{oi}(T) + RT\, ln\, P/P_o = \mu_i^*(T, P)\, , \qquad (15.12)_3$$

Eq.$(15.12)_1$ becomes Eq.(14.7) .

Equation $(15.12)_1$ shows that the chemical potential of a single component in a multicomponent ideal gas is equal to the chemical potential that *that* component would have if it were at the *same temperature* and the *reduced pressure* (i.e., the *partial pressure*), P_i.

For the standard chemical potential of the *i*th component we have either

$$\mu_i = u_{oi} - Ts_{oi} + RT_o + \int_{T_0}^{T} \frac{T' - T}{T'} c_{Pi}(T')\, dT' \qquad (15.12)_4$$

from Eq.(12.11)$_3$, or

$$\mu_{oi}(T) = u_{oi} - Ts_{oi} + \mathrm{R}T - \mathrm{R}T\, ln\, T/T_o) + \int_{T_o}^{T} \frac{T' - T}{T'}\, c_{Vi}(T')\, dT' \qquad (15.12)_5$$

from Eq.(12.11)$_4$.

The standard chemical potential of component i clearly does not depend on the composition and, in fact, remains the same when $\overline{n}_i \to 1$. Compliance with the sets of equations introduced above constitutes the *sufficient condition* for the ideal behavior of a multicomponent gas.

15.13 The Entropy and Free Enthalpy of Mixing of a Multicomponent Ideal Gas

Chapter 14 introduced the entropy of mixing of an ideal mixture but did not specify it explicitly. We are now ready to do this for the multicomponent ideal gas.

Equations (15.5)$_4$ and (15.6)$_4$ reduce to Eqs.(12.7)$_4$ and (12.8)$_4$ as $\overline{n}_i \to 1$. The terms $-\mathrm{R}\sum_i \overline{n}_i\, ln\, \overline{n}_i$ in these equations thus represent the difference between the entropies of a mixture of ideal gases and of a simple collection of individual ideal gases before they form a mixture. This difference therefore constitutes the *entropy of mixing*. Multiplying by N, we obtain

$$\Delta S_{\mathrm{mix}} = -\mathrm{R}\sum_i N_i\, ln\, \overline{n}_i \qquad (15.13)_1$$

as the entropy of mixing of a multicomponent ideal gas. Despite the minus sign in Eq.(15.12)$_1$, the entropy of mixing, ΔS_{mix}, is positive because any one of the $\overline{n}_i$'s is less than unity.

The athermal free enthalpy of mixing,

$$\Delta G_{\mathrm{mix}} = \mathrm{R}T\sum_i N_i\, ln\, \overline{n}_i\ . \qquad (15.13)_2$$

follows directly from Eq.(14.12)$_1$.

16. THE IDEAL SOLUTION

The concepts developed in the preceding two chapters can be extended from gaseous to condensed systems, i.e., to liquid and solid mixtures. Solutions are homogeneous mixtures formed by dissolving one or more substances, whether solid, liquid, or gaseous, in another substance. In a solution the mole fraction of one component, called the *solvent*, is generally much larger then the individual mole fractions of the other components, called the *solutes*. Although the solvent is usually a liquid, it equally can be a gas or a solid. In this case we speak of gaseous, or solid solutions. This chapter deals with liquid solutions only. More particularly, it considers *infinitely dilute solutions*, i.e., solutions in which the mole fraction of the solvent approaches unity. In contrast to the solvent, a *pure phase*, the solution constitutes a *mixed phase*.

16.0 Chapter Contents

16.1 The Ideal Solution

A solution becomes an *ideal solution* in the limit of *infinite dilution*. Designating the mole fraction of the solvent by $\overline{n}_1$, the condition of infinite dilution can be expressed as $\overline{n}_1 \to 1$ and is the analog of the conditions $T \to \infty$, $P \to 0$ for an ideal gas (cf. § 12). Being an ideal mixture, an ideal solution exhibits no volume change and no heat effects upon dilution in accordance with §§ 14.9 and 14.10.

16.2 The Fundamental Equation of the Ideal Solution

In the energy representation the fundamental equation of the ideal solution takes the form

$$U = (S, V, N_1, \ldots N_m \ldots) \qquad (16.2)_1$$

and in the entropy representation it becomes

$$S = (U, V, N_1, \ldots N_m \ldots) \tag{16.2)$_2$}$$

The subscript '1' on the mole numbers, N, traditionally refers to the solvent while the solutes take subscripts $m > 1$. The most frequently encountered ideal solution contains a single solute. The fundamental equations of the binary ideal solution therefore are

$$U = (S, V, N_1, N_2) \qquad (16.2)_3$$

and

$$S = (U, V, N_1, N_2)\,. \qquad (16.2)_4$$

in the energy, and the entropy representation, respectively.

In the absence of an explicit form for the fundamental equation of the ideal solution, we make use of the assumptions that the extensive variables are independent of each other (cf. § 11.2). The molar form of the *i*th component of the fundamental equation of the ideal solution in the entropy representation then becomes

$$s_i = s_{oi} + f(u_i) + \mathrm{R}\, ln v/v_i + \mathrm{R}\, ln \bar{\bar{n}}_i \qquad (16.2)_5$$

in analogy to the equation for the multicomponent ideal gas, Eq.(15.1).

16.3 The Equations of State of the Ideal Solution

The equations of state of the ideal solution are to all intents and purposes identical with those of the multicomponent ideal gas. The first again merely confirms that the internal energy of the ideal solution is a function of the temperature only. The second equation of state is still $Pv = \mathrm{R}T$. Equation (15.3) models the third equation of state of the *i*th component of the ideal solution.

16.4 The Chemical Potentials of the Ideal Solution

The chemical potential of the *i*th component of the ideal solution is the chemical potential of the *i*th component of the ideal mixture given by Eq.(14.7). Thus, it is

$$\mu_i = \mu_i^*(T, P) + \mathrm{R}T\, ln\, \bar{n}_i\,, \qquad (16.4)$$

where $\mu_i^*(T,\, P)$ is the chemical potential of the ith pure substance at the temperature and pressure of the solution. Equation (16.4) may be considered to be the defining equation of the ideal solution and constitutes a *sufficient condition* for its ideal behavior.

16.5 The Fundamental Equation of the Ideal Solution in Parametric Form

Because the internal energy of the ideal solution is a function of the temperature only, and its volume is deemed to be independent of the pressure, we may write

$$u_i = u_{\mathrm{o}i} + \int_{T_\mathrm{o}}^{T} c_{Vi}(T')\, dT' \qquad (16.5)_1$$

and

$$s_i = s_{\mathrm{o}i} + \int_{T_\mathrm{o}}^{T} \frac{c_{Vi}(T')}{T'}\, dT' - \mathrm{R}\, ln\, \overline{n}_i \qquad (16.5)_2$$

for the parametric forms of the fundamental equation of the *i*th component of the ideal solution.

Summing over all components yields

$$u = \sum\nolimits_i \overline{n}_i u_{\mathrm{o}i} + \sum\nolimits_i \overline{n}_i \int_{T_\mathrm{o}}^{T} c_{Vi}(T')\, dT' \qquad (16.5)_3$$

and

$$s = \sum\nolimits_i \overline{n}_i s_{\mathrm{o}i} + \sum\nolimits_i \overline{n}_i \int_{T_\mathrm{o}}^{T} \frac{c_{Vi}(T')}{T'}\, dT' - \mathrm{R} \sum\nolimits_i \overline{n}_i\, ln\, \overline{n}_i \qquad (16.5)_4$$

for the parametric molar forms of the fundamental equation if the ideal solution in terms of the heat capacities at constant volume, $c_{Vi}(T)$.

16.6 The Gibbs-Duhem Equation of the Ideal Solution

The integrated form of the Gibbs-Duhem equation for the ith component of an ideal solution becomes simply

$$s_i dT + \sum\nolimits_m N_{im}\, d\mu_{im} = 0\,. \qquad (16.6)$$

For the special case of the binary solution see § 14.14.

16.7 The Entropy of Mixing of the Ideal Solution

The ideal solution is an *athermal* solution whose entropy of mixing is given by

$$\Delta S_{mix} = -\,\mathrm{R} \sum\nolimits_i N_i\, ln\, \overline{n}_i \qquad (16.7)_1$$

in analogy to that of a multicomponent ideal gas. For a binary solution

$$\Delta S_{\text{mix}} = -\,\mathrm{R}\,(N_1\,ln\,\overline{n}_1 + N_2\,ln\,\overline{n}_2) \qquad (16.7)_2$$

(cf. § 14.12).

16.8 The Free Enthalpy of Dilution

The *partial molar entropy of the solvent* in an ideal solution is obtained by differentiating Eq.(15.12)₁ with respect to N_1. This yields

$$\Delta\overline{S}_1 = \frac{\partial\Delta S_{\text{mix}}}{\partial N_1} = -\,\mathrm{R}\,ln\,\overline{n}_1\,, \qquad (16.8)_1$$

and the *partial molar free enthalpy* then follows from

$$\Delta\overline{G}_1 = -\,\mathrm{R}T\Delta\overline{S}_1 \qquad (16.8)_2$$

as

$$\Delta\overline{G}_1 = \frac{\partial\Delta G_{\text{mix}}}{\partial N_1} = \mathrm{R}T\,ln\,\overline{n}_1\,. \qquad (16.8)_3$$

$\Delta\overline{G}_1$, called the *free enthalpy of dilution,* is the change in the free enthalpy of the solution when an additional mole of solvent is added to it. Since $0 < \overline{n}_1 < 1$, the free enthalpy of dilution is negative as required. In all three equations we have omitted the subscript 'mix' as unnecessary because partial molar quantities exist only in mixtures.

16.9 Solution Equilibrium and Free Enthalpy of Dilution

As solution takes place, the change in the chemical potential of the solvent, $\Delta\mu_1$, is given by

$$\Delta\mu_1 = \mu_1 - \mu_1^{\circ} \qquad (16.9)_1$$

where μ_1 is the chemical potential of the solvent in the solution, and μ_1° is the chemical potential of the pure solvent. We then have [cf. Eq.(14.8)],

$$\Delta\mu_1 = \left.\frac{\partial\Delta G}{\partial N_1}\right|_{T,\,P,\cdots N_{i(\neq 1)}\cdots} = \Delta\overline{G}_1 \qquad (16.9)_2$$

At equilibrium the chemical potential of the solvent in the solution and the chemical potential of the pure solvent must be equal. Thus, $\mu_1 = \mu_1^{\circ}$, and therefore the change in the free enthalpy of dilution vanishes, i.e.,

$$\Delta\overline{G}_1 = 0\,. \tag{16.9)$_3$}$$

Since, therefore, at equilibrium the change in the free enthalpy of the solution is zero when an additional mole of solvent is added to it, Eq.(16.9)$_3$ expresses the condition of *solution equilibrium*, i.e., the condition that the free enthalpy of the system be a minimum with respect to changes in the composition of the solution.

16.10 Solution Equilibrium and Vapor Pressure

The condition for two phases to be in equilibrium with respect to their composition is that their chemical potentials be the same (cf. §§ 19.16). At equilibrium the chemical potential of the ith component of the solution, μ_i^{sol}, and that of the vapor above it, μ_i^{vap}, must therefore be equal. Through the condition of *phase equilibrium*,

$$\mu_i^{\mathrm{sol}} = \mu_i^{\mathrm{vap}}, \qquad (16.10)_1$$

the equilibrium of an ideal solution can therefore be discussed thermodynamically in terms of the partial pressures in the saturated vapor as long as the vapor can be regarded as a multicomponent ideal gas. The chemical potential of the ith component of the vapor is then, in accordance with Eq.(15.12)$_1$, given by

$$\mu_i^{\mathrm{vap}} = \mu_{\mathrm{o}i}(T) + \mathrm{R}T\; ln\; P_i/P_{\mathrm{o}} \qquad (16.10)_2$$

where $\mu_{\mathrm{o}i}(T)$ is given by Eq.(15.12)$_5$.

16.11 Henry's Law

Substituting Eqs. (16.4)$_2$ and (16.10)$_2$ into the equilibrium condition, Eq.(16.10)$_1$, we find

$$\mu_i^*(T, P) + \mathrm{R}T\; ln\; \overline{n}_i = \mu_{\mathrm{o}i}(T) + \mathrm{R}T\; ln\; P_i/P_{\mathrm{o}}\,. \qquad (16.11)_1$$

or

$$\mu_i^*(T, P) - \mu_{\mathrm{o}i}(T) = \mathrm{R}T\; ln\; P_i/\overline{n}_i P_{\mathrm{o}} = \mathrm{R}T\; ln\; \mathrm{K}_i/P_{\mathrm{o}} \qquad (16.11)_2$$

where

$$P_i = \mathrm{K}_i\,\overline{n}_i \qquad (16.11)_3$$

P_i is the partial pressure of the ith component in the vapor. Equation (16.11)$_3$ is known as *Henry's Law* and expresses the proportionality of the vapor pressure of the ith component with its mole fraction in the ideal solution. K_i is referred to as *Henry's constant*. It is considered to be a constant because it is independent of composition although it depends on temperature and pressure, and should properly be denoted by $\mathrm{K}_i\,(T, P)$.

16.12 Raoult's Law

In the limit that $\overline{n}_i \to 1$, K$_i$ approaches P_i^o, the vapor pressure of the pure component i. The relation

$$P_i = P_i^o \overline{n}_i \tag{16.12$_1$}$$

is *Raoult's Law.* It defines ideal behavior in a solution in terms of the partial vapor pressure instead of the chemical potential [cf. Eq.(16.4)].

We note that by Raoult's Law the free enthalpy of dilution can be stated in terms of the vapor pressures as

$$\Delta\overline{G}_1 = \frac{\partial \Delta G_{\text{mix}}}{\partial N_1} = RT\, ln\, P_i/P_i^o\, . \tag{16.12$_2$}$$

Raoult's Law ultimately depends on the validity of Eq.(16.7)$_1$ which expresses the entropy of mixing in terms of the mole fractions. This assumes that the molecules of all components are of comparable (theoretically equal) size. If this is not the case, Raoult's Law fails (cf. § 16.17).

16.13 Colligative Properties

We may rewrite Raoult's Law, Eq.(16.12)$_1$, for the solvent in a binary solution as $P_1/P_1^o = \overline{n}_1 = 1 - \overline{n}_2$. Rearranging gives

$$\frac{P_1^o - P_1}{P_1^o} = \overline{n}_2. \tag{16.13}$$

Thus, the relative lowering of the vapor pressure of the pure solvent that occurs upon the introduction of the solute, equals the mole fraction of the solute.

Phenomena related to the relative lowering of the vapor pressure are the *depression of the freezing point*, the *elevation of the boiling point*, and the *osmotic pressure*. These phenomena are collectively referred to as *colligative properties*. Because they allow the experimental determination of the mole fraction of the solute, they form the basis of experimental methods for the determination of *molecular masses* (molecular weights).

16.14 The Osmotic Pressure

We single out the osmotic pressure from among the colligative properties for further discussion. Consider an ideal binary solution separated from the pure solvent by a membrane which is impermeable to the solvent and the solute alike. Both the pure solvent and the solution are in contact with a heat reservoir and are, therefore, at constant temperature T. They are not, however, in contact with a work reservoir.

In accordance with the dictum that matter flows from regions of high to regions of low chemical potential (cf. § 4.10), the chemical potential of the pure solvent at the pressure P, $\mu^*(P)$, is clearly higher than that of the solvent in the solution, $\mu_1^*(P)$, at the same pressure P. If now the membrane is made permeable with respect to the solvent, this will flow (diffuse) into the solution until partial equilibrium (i.e., thermal and diffusional equilibrium) is attained. At that point, however, mechanical equilibrium has *not* been reached. The pressures on both side of the membrane are different because the influx of solvent into the solution has created an extra hydrostatic pressure on the latter. The difference between the two pressures, the pressure, P^s, on the solution, and the pressure, P, on the solvent,

$$\Pi = P^s - P\,, \tag{16.14}$$

is called the *osmotic pressure*. It is the excess pressure that would have to be exerted on the solution to prevent any further diffusion of solute into it, thus assuring that the solution is in mechanical as well as thermal and diffusional equilibrium.

16.15 Osmotic Pressure and Solvent Concentration

We wish to relate the osmotic pressure to the solvent concentration, i.e., to the mole fraction of the solvent in the solution. The Maxwell relation listed as the third of Eqs.(10.6)$_4$ may be restated for the solvent as

$$\left.\frac{\partial \mu_1}{\partial P}\right|_{T,N} = \left.\frac{\partial V}{\partial N_1}\right|_{T,P}. \qquad (16.15)_1$$

The right-hand-side is equal to $\overline{V}_1$, the partial molar volume of the solvent in the solution. Inserting Eq.(16.4) into the left-hand-side yields

$$\left.\frac{\partial \mu^*(T,P)}{\partial P}\right|_{T,N} + \left.\frac{\partial \mathrm{R}T\ ln\ \overline{n}_1}{\partial P}\right|_{T,N} = \overline{V}_1 \qquad (16.15)_2$$

which we integrate between the pressures, P^s and P. This yields

$$\mathrm{R}T\ ln\ \overline{n}_1 = -\int_{P^s}^{P} \mu^*(T,P)dP' + \int_{P^s}^{P} \overline{V}_1 \mathrm{d}P'\,. \qquad (16.15)_3$$

Neglecting the compressibility of the solvent over the pressure range of interest, the first integral vanishes and the molar volume can be taken out from under the second integral sign. We then obtain

$$\mathrm{R}T\ ln\ \overline{n}_1 \simeq \overline{V}_1(P - P^s)\,, \qquad (16.15)_4$$

and the relation between the osmotic pressure and the mole fraction of the solvent becomes

$$\Pi \simeq -\frac{RT}{\overline{V}_1} \ln \overline{n}_1 . \qquad (16.15)_5$$

The osmotic pressure in an ideal solution is thus independent of the nature of the solute.

16.16 Osmotic Pressure and Solute Concentration – van't Hoff's Relation

Let us take another look at Eq.(16.15)$_5$. As $\overline{n}_1 \to 1$, we may write

$$\ln \overline{n}_1 = \ln(1 - \overline{n}_2) \simeq -\overline{n}_2, \qquad (16.16)_1$$

so that Eq.(16.15)$_5$ becomes

$$\Pi = \frac{RT\,\overline{n}_2}{\overline{V}_1} . \qquad (16.16)_2$$

But $\overline{n}_2 = N_2/N$, and in a very dilute solution $N = N_1 + N_2 \simeq N_1$, so that $\overline{V}_1 N = V_1$, the volume of the solvent in the solution. This is indistinguishable from V, the volume of the solution, when $\overline{n}_1 \to 1$. We therefore arrive at *van't Hoff's relation*,

$$\Pi = \frac{N_2 RT}{V} = RTc_2 \qquad (16.16)_3$$

since $N_2/V = c_2$, the volume concentration of the solute molecules. Thus in the limit of very dilute solution the osmotic pressure is independent of the nature of the solvent.

The relation bears a striking formal resemblance to the equation of state of an ideal gas, Eq.(12.2)$_4$. It must be noted, however, that ideal behavior in the sense of van't Hoff is a more stringent condition than ideal behavior in the sense of Raoult's Law. For van't Hoff's relation to be valid, the solution needs to be more dilute than is necessary for ideal behavior in general.

Because $M_2 = c_2 V/N_2$, where M_2 is the molecular mass of the solute, van't Hoff's relation may be used in the determination of the molecular masses of small molecules by *osmometry*, the measurement of the osmotic pressure.

16.17 The Entropy and Free Enthalpy of Mixing of Macromolecular Solutions

Ideal behavior in the sense of Raoult's Law (§ 16.12) requires that both solvent and solute molecules be of closely comparable size. This assumption is reasonable when one considers gas molecules and remains reasonable for many solvent-solute systems. However, even extremely dilute solutions of *macromolecules* (long chain molecules) depart strongly from ideal behavior in the sense of Raoult's Law when their behavior is examined in terms of mole fractions. A better form of the entropy of mixing for a solution of macromolecules comes from the Flory-Huggins theory[13] (cf. p. 126) that takes into account the disparity between the size of a solvent molecule and the size of a long-chain molecule. It considers the chain to consists of x *solvent-sized segments*. The expression for the entropy of mixing then takes the form

$$\Delta S_{\text{mix}} = -\text{R}\,(N_1 \, \mathit{ln}\, \bar{v}_1 + N_2 \, \mathit{ln}\, \bar{v}_2)\,. \tag{16.17$_1$}$$

where

$$\bar{v}_1 = \frac{N_1}{N_1 + xN_2} \qquad \text{and} \qquad \bar{v}_2 = \frac{xN_2}{N_1 + xN_2}\,. \tag{16.17$_2$}$$

are the volume fractions of the solvent, and the macromolecular solute, respectively. Equation (16.17)$_1$ is valid in this form in the absence of any enthalpy change on dilution [cf. § 17.24 for the addition of an extra term taking account essentially of changes in the free enthalpy of dilution]. .

Thus, when the solvent and solute molecules are of dissimilar size, the mole fractions must be replaced by the volume fractions. We note that Eq.(16.17)$_1$ is the more general expression and comprises the equation

$$\Delta S_{\text{mix}} = -\text{R}\,(N_1 \, \mathit{ln}\, \bar{n}_1 + N_2 \, \mathit{ln}\, \bar{n}_2), \tag{16.17$_3$}$$

valid for small solute molecules [cf. Eq.(16.7)$_2$], as a special case when $x = 1$.

From Eq.(16.17)$_3$the free enthalpy of mixing follows as

$$\Delta G_{\text{mix}} = \text{R}T(N_1 \, \mathit{ln}\, \bar{v}_1 + N_2 \, \mathit{ln}\, \bar{v}_2) \tag{16.17$_4$}$$

for of a solution of macromolecules.

17. THE IDEAL RUBBER

This chapter discusses rubber as an example of a homogeneous non-crystalline solid that provides an example of a single-component thermodynamic system whose fundamental equation is characterized by four, not three, extensive variables. The formalism developed here thus serves as a model for systems in which surface effects cannot be neglected or which are acted on, for instance, by electrical, magnetic, or gravitational fields.

The first three sections contain some needed background information. They are followed by fourteen sections dealing with rubbers at constant composition, i.e., with *unswollen rubbers*. The last two of these sections are concerned with the *ideal rubber*, an example of an ideal solid system. The final five sections tackle the thermodynamics of swelling and of *swollen rubbers*. Rubbers generally swell in organic liquids. However, swelling phenomena are also of great importance in tissues and other biological materials were water is the swelling liquid.

17.0 Chapter Contents

17.1 The General Solid

In a fluid (a gas or a liquid) no definite relations exist between the various parts of the matter of which the fluid consists. Consequently, the mechanical distortion (change in *shape*) of a fluid requires no work and only its compression (change in *size*, i.e. volume) is of interest thermodynamically. In the thermodynamics of fluids, therefore, shape is a neutral property (§ 1.10). In the thermodynamics of solids, by contrast, we must consider the total work required to change both shape and size, i.e. the mechanical work of deformation. In the energy representation the Euler equation for a single-component homogeneous general solid therefore becomes

$$U = TS + \sum\nolimits_n \sigma_n(V_o\varepsilon_n) + \mu N \tag{17.1}$$

where σ_n and ε_n represent the six independent components of the symmetric second-order stress and strain tensors, respectively. The stress tensor components have the dimensions of force per unit area and are intensive quantities. The strain tensor components are dimensionless and are rendered extensive through multiplication by the initial (undeformed) volume, V_o.

17.2 The Isotropic Solid

A solid whose properties are the same in all three of the principal directions is called *isotropic*. Writing f_i for the forces and L_i for the extensions in the three principal directions, the Gibbs equation of such a solid becomes[10]

$$dU = TdS - PdV + \sum\nolimits_i f_i dL_i + \mu dN \,. \qquad \mathrm{i} = 1,2,3 \quad (17.2)_1$$

A further simplification results from the consideration that, if the solid is isotropic, all the thermodynamic information on its mechanical behavior can be obtained from experiments in *simple tension*, also called *uniaxial tension*. In this deformation a force, f, (or an extension, L) is applied in only one direction and the resulting extension (or force) is measured. Since the forces in the other two directions are zero, Eq.(17.2)$_1$ becomes simply

$$dU = TdS - PdV + fdL + \mu dN \qquad (17.2)_2$$

and the Euler equation in the energy representation takes the form

$$U = TS - PV + fL + \mu N \,. \qquad (17.2)_3$$

Because of the presence of the fL term in this equation, a crosslinked rubber furnishes an example of a non-simple system [cf. Eq.(8.19)].

17.3 Rubbers (Elastomers)

Rubbers, also called *elastomers*, form a class of rather unique solids. They are organic materials consisting of long, flexible chains of macromolecules crosslinked somewhat loosely to form a three-dimensional network. Thus, a rubber is theoretically one giant molecule. Because of the presence of the crosslinks, rubbers are capable of very large

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[10] see Sharda and Tschoegl (1974)

(up to ~ 1000%) *reversible deformations* and will not dissolve but will *swell* in a suitable solvent. Above the so-called *glass transition temperature* the chains possess sufficient mobility to impart to a rubber some of the characteristics of a liquid (e.g., relative incompressibility; see § 17.12).

Any real elastomer is an *imperfect network* that contains certain network defects. Such defects are *loose ends*, i.e., chains that are connect to the network at one end only, *physical entanglements*, i.e., chains looping over others, and *closed loops* resulting from linkages of two points on a single chain. There may also be present chains that are not tied to the network. Our concern here is with a *perfect network* that is deemed not to contain any network imperfections.

17.4 The Fundamental Equation of an Elastomer

In the energy representation the fundamental equation of an elastomer is thus given by

$$U = U(S, V, L, N) \tag{17.4}$$

where the number of moles, N, is interpreted as the number of moles of network chains. The number of canonical variables being 4, the number of degrees of freedom becomes 3 [cf. Eq.(8.7)].

In the absence of swelling an elastomer is at *constant composition*. We proceed to examine the alternative thermodynamic potentials of an elastomer under this aspect.

17.5 Alternative Thermodynamic Potentials for Elastomers

With 3 degrees of freedom, an elastomer in simple tension has $2^{f+1} - 2 = 14$ alternative thermodynamic potentials. At *constant composition* this number is halved (cf. § 8.7) and the total number of thermodynamic potentials of interest therefore becomes $7 + 1 = 8$. The seven alternative potentials to consider are

$$F = U[T] = U - TS\,, \tag*{(17.5)$_{1.1}$}$$
$$H = U[P] = U + PV, \tag*{(17.5)$_{1.2}$}$$
$$D = U[f] = U - fL\,, \tag*{(17.5)$_{1.3}$}$$
$$G = U[T, P] = U - TS + PV\,, \tag*{(17.5)$_{1.4}$}$$
$$B = U[T, f] = U - TS - fL\,, \tag*{(17.5)$_{1.5}$}$$
$$E = U[P, f] = U + PV - fL\,, \tag*{(17.5)$_{1.6}$}$$
$$Z = U[T,.P, f] = U - TS + PV - fL\,, \tag*{(17.5)$_{1.7}$}$$

and the alternative fundamental equations follow as

$$F = F(T, V, L, N)\,, \tag*{(17.5)$_{2.1}$}$$
$$H = H(S, P, L, N)\,, \tag*{(17.5)$_{2.2}$}$$
$$D = D(S, V, f, N)\,, \tag*{(17.5)$_{2.3}$}$$
$$G = G(T, P, L, N)\,, \tag*{(17.5)$_{2.4}$}$$
$$B = B(T, V, f, N)\,, \tag*{(17.5)$_{2.5}$}$$
$$E = E(S, P, f, N)\,, \tag*{(17.5)$_{2.6}$}$$
$$Z = Z(T, P, f, N)\,. \tag*{(17.5)$_{2.7}$}$$

In addition to Eqs.$(17.2)_2$and $(17.2)_3$ for the internal energy the seven alternative Gibbs equations in the energy representation then become

$$dF = -SdT - PdV + fdL + \mu dN \,, \qquad (17.5)_{3.1}$$
$$dH = TdS + VdP + fdL + \mu dN \,, \qquad (17.5)_{3.2}$$
$$dD = TdS - PdV - Ldf + \mu dN \,, \qquad (17.5)_{3.3}$$
$$dG = -SdT + VdP + fdL + \mu dN \,, \qquad (17.5)_{3.4}$$
$$dB = -SdT - PdV - Ldf + \mu dN \,, \qquad (17.5)_{3.5}$$
$$dE = TdS + VdP - Ldf + \mu dN \,, \qquad (17.5)_{3.6}$$
$$dZ = -SdT + VdP + Ldf + \mu dN \,, \qquad (17.5)_{3.7}$$

while the seven Euler equations in the same representation take the forms

$$F = -PV + fL + \mu N \,, \qquad (17.5)_{4.1}$$
$$H = TS + fL - \mu N \,, \qquad (17.5)_{4.2}$$
$$G = fL + \mu N \,, \qquad (17.5)_{4.3}$$
$$D = TS - PV + \mu N \,, \qquad (17.5)_{4.4}$$
$$B = -PV + \mu N \,, \qquad (17.5)_{4.5}$$
$$E = TS + \mu N \,, \qquad (17.5)_{4.6}$$
$$Z = \mu N \,. \qquad (17.5)_{4.7}$$

The potential functions U, F, H, and G differ from those in use in the thermodynamics of fluids in the additional fL terms. F, H, and G measure the work available in a reversible process from an elastomer at constant temperature, at constant pressure, and at constant temperature and pressure, respectively.

D and E measure the work available in a reversible process from an elastomer at constant force, and at constant pressure and force, respectively. B and Z measure the work available in a reversible process from an elastomer at constant temperature and force, and at constant temperature, pressure and force, respectively. B and Z are the free energies associated with D and E. Of the four, E and Z may respectively be called *elasthalpy* and *free elasthalpy*, but no special terms have come into use for D and B which are seldom used.

17.6 The Fundamental Set of Second-order Partial Derivatives of an Elastomer

In simple tension the internal energy of an elastomer at constant composition is $U = U(S, V, L)$. It thus has $\mathrm{f}+1=3$ first-order, and $\frac{1}{2}(\mathrm{f}+1)(\mathrm{f}+2)=6$ second-order partial derivatives.

The first order derivatives are

$$\left.\frac{\partial U}{\partial S}\right|_{V,L} = T, \qquad \left.\frac{\partial U}{\partial V}\right|_{S,L} = -P, \qquad \text{and} \qquad \left.\frac{\partial U}{\partial L}\right|_{S,V} = f,$$

and the fundamental set becomes

$$\left.\frac{\partial S}{\partial T}\right|_{V,L} = C_{V,L}/T, \qquad \left.\frac{\partial V}{\partial T}\right|_{V,L} = V\alpha_{S,L}, \qquad -\left.\frac{\partial V}{\partial P}\right|_{S,L} = V\kappa_{S,L} \qquad (17.6)_1$$

and

$$\left.\frac{\partial L}{\partial f}\right|_{S,V} = L\rho_{S,V}, \qquad \left.\frac{\partial L}{\partial T}\right|_{S,V} = L\beta_{S,V}, \qquad -\left.\frac{\partial L}{\partial P}\right|_{S,V} = L\chi_{S,V}\,. \qquad (17.6)_2$$

The first three coefficients are familiar except that they are now taken at constant length in addition to constant volume or constant entropy. Thus $C_{V,L}$ is the heat capacity at constant volume and length, and $\alpha_{S,L}$ and $\kappa_{S,L}$ are the adiabatic expansivity and adiabatic compressibility at constant length.

The next three coefficients are new. They represent the adiabatic change in length at constant volume as a function of the force, the temperature, and the pressure, respectively. In particular, $\rho_{S,V}$ is the adiabatic-isochoric length-force coefficient per unit length, $\beta_{S,V}$ is the adiabatic-isochoric length-temperature coefficient per unit length and, finally, $\chi_{S,V}$ is the adiabatic-isochoric linear compressibility. The requirement of adiabaticity and that of constant volume (which demands the application of a hydrostatic pressure), place severe experimental restrictions on the experimental determination of these coefficients.

17.7 The Primary Set of Second-order Partial Derivatives of an Elastomer

For an elastomer the appropriate potential from which to derive the primary set of second-order partial derivatives is the free elasthalpy, Z, since it is this potential that has all the intensive parameters as canonical variables. At constant composition we consider $Z = Z(T,\ P,\ f)$ and the three first-order partial derivatives become

$$\left.\frac{\partial Z}{\partial T}\right|_{P,f} = -S, \qquad \left.\frac{\partial Z}{\partial P}\right|_{T,f} = V, \qquad \left.\frac{\partial Z}{\partial f}\right|_{T,P} = -L\,.$$

The primary set then follows as:

$$\left.\frac{\partial S}{\partial T}\right|_{P,f} = C_{P,f}/T, \qquad \left.\frac{\partial V}{\partial T}\right|_{P,f} = V\alpha_{P,f}, \qquad \left.\frac{\partial V}{\partial P}\right|_{T,f} = -V\kappa_{T,f} \qquad (17.7)_1$$

and

$$\left.\frac{\partial L}{\partial f}\right|_{T,P} = L\rho_{T,P}, \qquad \left.\frac{\partial L}{\partial T}\right|_{P,f} = L\beta_{P,f}, \qquad -\left.\frac{\partial L}{\partial P}\right|_{T,f} = L\chi_{T,f}\,. \qquad (17.7)_2$$

Again, the first three coefficients are the familiar isobaric heat capacity, isobaric expansivity, and isothermal compressibility, all now at constant force. The three new coefficients represent changes in length with respect to force, temperature, or pressure, while the other two intensive parameters are held constant. In particular, $\rho_{T,P}$ is the isothermal-isobaric length-force coefficient per unit length, $\beta_{P,f}$ is the isobaric length-temperature coefficient per unit length at constant force, and $\chi_{T,f}$ is the linear isothermal compressibility, also at constant force.

17.8 'Hybrid' Primary Sets of Second-order Partial Derivatives for an Elastomer

Experimentally, changes at constant length are also important. The second-order partial derivatives of the free enthalpy at constant length, $G = G(T, P, L)$, furnish a 'hybrid' primary set of derivatives in which the length, L, an extensive parameter, replaces the force, f, an intensive parameter, in the canonical variables of the elasthalpy. We have

$$\left.\frac{\partial S}{\partial T}\right|_{P,L} = C_{P,L}/T, \qquad \left.\frac{\partial V}{\partial T}\right|_{P,L} = V\alpha_{P,L}, \qquad \left.\frac{\partial V}{\partial P}\right|_{T,L} = -V\kappa_{T,L} \qquad (17.8)_1$$

and

$$\left.\frac{\partial f}{\partial L}\right|_{T,P} = 1/L\rho_{T,P}, \qquad \left.\frac{\partial f}{\partial T}\right|_{P,L} = \psi_{P,L}, \qquad \left.\frac{\partial f}{\partial P}\right|_{T,L} = \zeta_{T,L} \, . \qquad (17.8)_2$$

where $C_{P,L}$ is the isobaric heat capacity at constant length, $\alpha_{P,L}$ is the isobaric expansivity at constant length, and $\kappa_{T,L}$ is the isothermal compressibility, also at constant length. The reciprocal of $\rho_{T,P}$ has been discussed in the preceding paragraph. The last two coefficients are the isobaric force-temperature coefficient at constant length, $\psi_{P,L}$, and the isothermal force-pressure coefficient at constant length, $\zeta_{T,L}$.

The remaining thermodynamic potentials also furnish 'hybrid' sets of second-order partial derivatives (cf. § 10.7). An important (and experimentally useful) one is the pressure-temperature coefficient at constant volume and length,

$$\gamma_{V,L} = \left.\frac{\partial P}{\partial T}\right|_{V,L} = \alpha_{P,L}/\kappa_{T,L} \qquad (17.8)_3$$

[cf. Eq.(10.5)$_2$] because neither $\alpha_{P,L}$, nor $\kappa_{T,L}$ require measurements at constant volume.

17.9 The Maxwell Relations for Elastomers

By §§ 8.6 and 8.7, at constant composition an elastomers with 3 degrees of freedom possesses a total of $\frac{1}{2}(2^{f+1} - 2) + 1 = 2^f = 8$ thermodynamic potentials, and $\frac{1}{4}f(f+1) = 3$ 'mixed' second order partial derivatives for each potential. The number of Maxwell relations therefore is 24. The complete set is assembled below.

U:

$$\left.\frac{\partial T}{\partial V}\right|_{S,L} = -\left.\frac{\partial P}{\partial S}\right|_{V,L}, \qquad \left.\frac{\partial T}{\partial L}\right|_{S,V} = \left.\frac{\partial f}{\partial S}\right|_{L,V}, \qquad -\left.\frac{\partial P}{\partial L}\right|_{V,S} = \left.\frac{\partial f}{\partial V}\right|_{L,S} \qquad (17.9)_1$$

F:

$$\left.\frac{\partial S}{\partial V}\right|_{T,L}=\left.\frac{\partial P}{\partial T}\right|_{V,L},\quad -\left.\frac{\partial S}{\partial L}\right|_{T,V}=\left.\frac{\partial f}{\partial T}\right|_{L,V},\quad -\left.\frac{\partial P}{\partial L}\right|_{V,T}=\left.\frac{\partial f}{\partial V}\right|_{L,T}\qquad (17.9)_2$$

H:

$$\left.\frac{\partial T}{\partial P}\right|_{S,L}=\left.\frac{\partial V}{\partial S}\right|_{P,L},\quad \left.\frac{\partial T}{\partial L}\right|_{S,P}=\left.\frac{\partial f}{\partial S}\right|_{L,P},\quad \left.\frac{\partial V}{\partial L}\right|_{P,S}=\left.\frac{\partial f}{\partial P}\right|_{L,S}\qquad (17.9)_3$$

G:

$$-\left.\frac{\partial S}{\partial P}\right|_{T,L}=\left.\frac{\partial V}{\partial T}\right|_{P,L},\quad -\left.\frac{\partial S}{\partial L}\right|_{T,P}=\left.\frac{\partial f}{\partial T}\right|_{L,P},\quad \left.\frac{\partial V}{\partial L}\right|_{P,T}=\left.\frac{\partial f}{\partial P}\right|_{L,T}\qquad (17.9)_4$$

D:

$$\left.\frac{\partial T}{\partial V}\right|_{S,f}=-\left.\frac{\partial P}{\partial S}\right|_{V,f},\quad \left.\frac{\partial T}{\partial f}\right|_{S,V}=-\left.\frac{\partial L}{\partial S}\right|_{f,V},\quad \left.\frac{\partial P}{\partial f}\right|_{V,S}=\left.\frac{\partial L}{\partial V}\right|_{f,S}\qquad (17.9)_5$$

B:

$$\left.\frac{\partial S}{\partial V}\right|_{T,f}=\left.\frac{\partial P}{\partial T}\right|_{V,f},\quad \left.\frac{\partial S}{\partial f}\right|_{T,V}=\left.\frac{\partial L}{\partial T}\right|_{f,V},\quad \left.\frac{\partial P}{\partial f}\right|_{V,T}=\left.\frac{\partial L}{\partial V}\right|_{f,T}\qquad (17.9)_6$$

E:

$$\left.\frac{\partial T}{\partial P}\right|_{S,f}=\left.\frac{\partial V}{\partial S}\right|_{P,f},\quad \left.\frac{\partial T}{\partial f}\right|_{S,P}=-\left.\frac{\partial L}{\partial S}\right|_{f,P},\quad \left.\frac{\partial V}{\partial f}\right|_{P,S}=-\left.\frac{\partial L}{\partial P}\right|_{f,S}\qquad (17.9)_7$$

Z:

$$\left.\frac{\partial V}{\partial T}\right|_{P,f}=-\left.\frac{\partial S}{\partial P}\right|_{T,f},\quad \left.\frac{\partial S}{\partial f}\right|_{T,P}=\left.\frac{\partial L}{\partial T}\right|_{f,P},\quad \left.\frac{\partial L}{\partial P}\right|_{f,T}=-\left.\frac{\partial V}{\partial f}\right|_{P,T}\qquad (17.9)_8$$

The potentials from which the relations are derived are again listed in the left margin in bold font.

17.10 The Chemical Potential of an Elastomer

The statement is often seen that the chemical potential equals the molar Gibbs potential, i.e., g, the molar free enthalpy [cf. Eq.(14.2)$_6$]. In the thermodynamic simple system the canonical variables of G are the intensive parameters of the system apart from the mole number, N. In an elastomer, however, the chemical potential is given, in analogy to § 8.24, by

$$\left.\frac{\partial U}{\partial N}\right|_{S,V,L}=\left.\frac{\partial H}{\partial N}\right|_{S,P,L}=\left.\frac{\partial F}{\partial N}\right|_{T,V,L}=\left.\frac{\partial G}{\partial N}\right|_{T,P,L}=\mu\qquad (17.10)_1$$

from the first four thermodynamic potentials, and

$$\left.\frac{\partial D}{\partial N}\right|_{S,V,f}=\left.\frac{\partial B}{\partial N}\right|_{T,V,f}=\left.\frac{\partial E}{\partial N}\right|_{S,P,f}=\left.\frac{\partial Z}{\partial N}\right|_{T,P,f}=\mu \qquad (17.10)_2$$

from the last four. Thus, the chemical potential of an elastomer is the same as the molar free enthalpy when taken *at constant length.* If one wishes to equate the chemical potential of a rubber to that molar thermodynamic potential whose canonical variables, apart from the mole number, are the complete set of intensive parameters, one must turn to the free elasthalpy. We have

$$\mu=\left.\frac{\partial Z}{\partial N}\right|_{T,P,f}=Z/N=z\,, \qquad (17.10)_3$$

where z is the molar free elasthalpy.

17.11 The Gibbs-Duhem Equation for Elastomers

As the complete Legendre transform of the internal energy, $U=U(S,V,L,N)$, the Gibbs-Duhem equation for an elastomer becomes

$$SdT-VdP+Ldf+Nd\mu=0 \qquad (17.11)$$

in the energy representation.

17.12 The Assumption of Incompressibility

At constant composition, an elastomer possesses the three equations of state

17.13 The Ideal Rubber

Ideal behavior, as defined in § 11.2, requires that, at constant composition, each equation of state depend on only one extensive parameter. Thus, Eqs.(17.12)$_2$ must become

$$\frac{1}{T} = \frac{1}{T}(U) \qquad \text{and} \qquad \frac{f}{T} = \frac{f}{T}(L) \tag{17.13}$$

and these equations represent necessary conditions for the ideal behavior of a rubber. An ideal rubber is, of course, necessarily also a *perfect* rubber (cf. § 17.3).

17.14 The Equations of State of the Ideal Rubber

The second of Eqs.(17.12)$_2$ is commonly called simply *THE equation of state* of the ideal rubber. An explicit form for it cannot be derived within thermodynamic theory. The statistical mechanical theory of rubber elasticity[11] furnishes

$$f = \mathrm{A_o}\nu_e\mathrm{R}T(\lambda - \lambda^{-2})\,,. \qquad (17.14)_1$$

where $\mathrm{A_o}$ is the initial (i.e. undeformed) cross-sectional area on which the force, f, acts, and $\lambda = L/L_o$, where L_o is the initial (undeformed) length, is called the *stretch ratio*. R is the universal gas constant, and ν_e is the *crosslink density*, i.e., the number of moles of effective network chains per unit volume. Hence, the second equation of state,

$$\frac{f}{T} = \mathrm{A_o}\nu_e\mathrm{R}\left[\frac{L}{L_o} - \frac{L_o^2}{L^2}\right] \qquad (17.14)_2$$

is more appropriately called the *mechanical equation of state* of the ideal rubber. This is seen, as required, to depend on L only since ν_e, of course, does not depend on λ.

The first of Eqs.(17.13) asserts that the internal energy must depend on the temperature only. This can be expressed as

$$\left.\frac{\partial U}{\partial L}\right|_{T,V} = 0 \qquad (17.14)_3$$

or, in words, that at constant temperature and volume, U does not depend on L.

We note that Eq.(17.14)$_3$ parallels the requirement that

$$\left.\frac{\partial U}{\partial V}\right|_{T} = 0 \qquad (17.14)_4$$

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[11] see, e.g., Treloar (1975), pp. 42-100; Mark and Erman (1988), pp.7-21.

for an ideal gas, since the internal energy of an ideal gas also is a function of the temperature only (cf. § 12.2).

17.15 The Fundamental Equation of the Ideal Rubber

The fundamental equation of an ideal rubber in simple tension becomes $S = S(U, L)$ in the entropy representation because at constant composition U and L are its only canonical variables. To express the fundamental equation in parametric form we integrate the Gibbs equation

$$dS = \frac{1}{T}\,dU - \frac{f}{T}\,dL \tag{17.15$_1$}$$

after suitable substitutions for dU and f/T. Because U depends only on the temperature, we have $dU = C_{V,L}(T)\,dT$. Considering the heat capacity to be constant over the temperature range required, this simplifies to

$$dU = C_{V,L}\,dT \tag{17.15$_2$}$$

and integration yields

$$U = C_{V,L}\,(T - T_o)\,. \tag{17.15$_3$}$$

Inserting this as well as Eq.(17.14)$_2$ into Eq.(17.15)$_1$, integration produces

$$S \;=\; S_o + C_{V,L}\;ln\,T/T_o - \frac{1}{2}N\mathrm{R}(\lambda^2 + 2\lambda^{-1}) \tag{17.15$_4$}$$

since $A_o L_o \nu_e = V_o \nu_e = N$ is the number of moles of network chains. Equations (17.15)$_3$ and (17.15)$_4$ are the parametric equations for the fundamental equation of an ideal rubber. They constitute another example of an explicit form of a fundamental equation (cf. § 13.1), albeit in parametric form.

17.16 The Chemical Potential of the Ideal Rubber

Substituting Eq.(17.15)$_2$ into the first of Eqs.(17.10)$_1$ we obtain the chemical potential of an ideal rubber as

$$\mu = \left.\frac{\partial U}{\partial N}\right|_{S,L} = c_{V,L}T. \tag{17.16}$$

By Eq.(11.3)$_1$ behavior in accordance with the above is a sufficient condition for the ideal behavior of a rubber.

17.17 The Shear Modulus of the Ideal Rubber

Appendix 5 presents the derivation of the mechanical equation of state by the methods of continuum mechanics. This derivation does not make any assumptions concerning the structure of the material as a three-dimensional network of flexible chains. It yields the equation in the form

$$\sigma = G(\lambda - \lambda^{-2}) \qquad (17.17)_1$$

where $\sigma = f/A_o$ is the stress in simple tension and G is the shear modulus of the rubber. The latter is an important parameter in the theory of the rheological behavior of rubber. Classical elasticity theory defines the shear modulus as $\sigma = G\epsilon$, where ϵ is the *hookean strain,* i.e., the strain in infinitesimal deformation, also called the *Cauchy strain.* By contrast, $\lambda - \lambda^{-2}$ above, also called the *neohookean strain,* is a strain in large deformation. Experimentally, Eq.$(17.17)_1$ commonly holds only for about 20-40% extensions, depending on the type of rubber, but this is significantly larger then the deformations other materials can be subjected to without causing rupture or irreversible *plastic* changes in shape (flow).

In continuum mechanics Eq.$(17.17)_1$ represents a *constitutive equation,* i.e., an equation linking a measure of stress and a measure of strain through a material property characteristic of the constitution of matter, here the shear modulus, G. Comparison of Eqs.$(17.17)_1$ and $(17.14)_1$ identifies the latter as

$$G = \nu_e RT = \rho RT/M_c\,. \qquad (17.17)_2$$

This claims that the modulus is directly proportional to the (absolute) temperature, and also directly proportional to the crosslink density, ν_e. It is also inversely proportional to M_c, the number average molecular mass (molecular weight) of the chains, ρ being the density of the rubber. The modulus may be obtained in a number of ways. The simplest one of these is the measurement of σ as a function of $\lambda - \lambda^{-2}$ and taking the slope of the initial, straight-line portion of the plot. For an estimate of ν_e from swelling measurements see § 17.24.

17.18 The Elastic Restoring Force

The original length, L_o, of a piece of ideal rubber that has been stretched to the new length, L, is completely recovered once the force, f, is removed. The process of deformation is therefore a purely *elastic* one (the applied force has experienced no *viscous dissipation* of the energy of deformation). Thus, the force responsible for restoring the original shape is identical with the force required to deform the material, and f is also called the *elastic restoring force.*

At constant composition, i.e., at any given crosslink density, we obtain f as

$$f = \left.\frac{\partial F}{\partial L}\right|_{T,V}, \qquad (17.18)_1$$

from Eq.$(17.5)_{3,1}$, and using $F = U - TS$. Hence we may write

$$f = \left.\frac{\partial U}{\partial L}\right|_{T,V} - T\left.\frac{\partial S}{\partial L}\right|_{T,V} = f_{\mathrm{u}} + f_{\mathrm{s}} \qquad (17.18)_2$$

where

$$f_{\mathrm{u}} = \left.\frac{\partial U}{\partial L}\right|_{T,V} \qquad (17.18)_3$$

is the *internal energy contribution* to the elastic restoring force in the rubber, while

$$f_{\mathrm{s}} = -T\left.\frac{\partial S}{\partial L}\right|_{T,V} = T\left.\frac{\partial f}{\partial T}\right|_{V,L} \qquad (17.18)_4$$

is the *entropic contribution.* The second of the latter equations follows from the second of the Maxwell relations referenced as Eqs.$(17.9)_2$.

In an ideal rubber the restoring force results purely from entropy changes since $f_{\mathrm{u}} = 0$ by Eq.$(17.14)_3$. The statistical mechanical theory of rubber elasticity shows that these entropy changes are changes in the configurational entropy of the chains, brought about by the imposed deformation[11] (cf. p. 121).

17.19 The Relative Internal Energy Contribution to the Elastic Restoring Force

The relative contribution, f_{u}/f, of the internal energy to the elastic restoring force in a rubber, is of some theoretical as well as experimental interest. From $f_{\mathrm{u}} = f - f_{\mathrm{s}}$, using Eq.$(17.18)_4$, we obtain this ratio as

$$\frac{f_{\mathrm{u}}}{f} = 1 - \frac{T}{f}\left.\frac{\partial f}{\partial T}\right|_{V,L} . \qquad (17.19)_1$$

The experimental determination of the force-temperature coefficient at constant volume is difficult. It is possible, however, to make use of the thermodynamic identity

$$\left.\frac{\partial f}{\partial T}\right|_{V,L} = \left.\frac{\partial f}{\partial T}\right|_{P,L} + \left.\frac{\partial P}{\partial T}\right|_{V,L}\left.\frac{\partial f}{\partial P}\right|_{T,L} \qquad (17.19)_2$$

to replace the coefficient at constant volume with that at constant pressure. Using Eqs.$(17.19)_2$ and $(17.8)_3$, we find

$$\frac{f_{\mathrm{u}}}{f} = 1 - \frac{T}{\mathrm{f}}\left.\frac{\partial f}{\partial T}\right|_{P,L} - \gamma_{V,L}\left.\frac{\partial f}{\partial P}\right|_{T,L} \qquad (17.19)_3$$

where

$$\gamma_{V,L} = \left.\frac{\partial P}{\partial T}\right|_{V,L} = \frac{\alpha_{P,L}}{\kappa_{T,L}}\,, \tag{17.19$_4$}$$

is the pressure-temperature coefficient at constant volume and length which conveniently does not require measurements at constant volume [cf. Eq.(17.8)$_3$].

17.20 Swelling

Hitherto we have discussed the thermodynamics of rubber under the assumption of constant composition. This assumption is no longer tenable when a piece of rubber is immersed in a solvent. It then changes its composition because it *swells*, i.e., it imbibes a certain amount of the solvent. It cannot dissolve (cf. § 17.3) because the network chains are held together by the crosslinks.

The fundamental equation of a swollen elastomer becomes

$$U = U(S, V, L, N_1, N_2) \tag{17.20}$$

where N_1 and N_2 are respectively the number of moles of solvent molecules and of network chains[12].

The process of swelling has much in common with the process of solution. Both processes are concerned with the equilibrium between a pure and a mixed phase. In the latter case the pure phase is (generally) solid (the solute) and the mixed phase is liquid (the solution). In the former case the situation is reversed: the pure phase is liquid (the swelling agent, that is, the solvent) and the mixed phase is solid (the swollen rubber, a gel). Thermodynamically the difference is irrelevant.

17.21 The Free Enthalpy of Dilution of a Swollen Rubber

In terms of the vapor pressures the free enthalpy of dilution upon swelling is, in analogy to Eq.(16.12)$_2$ for a solution, given by

$$\Delta G_1 = \frac{\partial \Delta G_{\text{sw}}}{\partial N_1} = \mathrm{R}T\,ln\;P/P^{\mathrm{o}} \tag{17.21}$$

where P is the vapor pressure of the solvent in the swollen rubber and P^{o} is the vapor pressure of the pure solvent. We have omitted the bar over G, and the subscript on the pressures since only the solvent has an appreciable vapor pressure. At equilibrium, $P = P^{\mathrm{o}}$, since $\Delta G_1 = 0$. Thus, the equilibrium degree of swelling is the same whether the piece or rubber is immersed in the solvent or is exposed to the saturated vapor.

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[12] N_2 is $V_{\mathrm{o}}\,\nu_{\mathrm{c}}$ where ν_{c} is the *crosslink density* (cf. § 17.14).

17.22 The Swelling Pressure

Equation $(16.15)_5$ for the osmotic pressure in a solution is applicable also to a swollen rubber. Thus, we have

$$\Pi \simeq -\frac{RT}{v_1} \ln \bar{n}_1 \tag{17.22)$_1$ (}$$

where v_1 is the molar volume of the solvent, and Π is called the *swelling pressure*. It is the excess pressure that must be applied to the swollen rubber to ensure that it is in mechanical as well as thermal and diffusional equilibrium with the pure solvent. In dealing with osmotic pressure we consider a solution that is separated from the solvent by a semi-permeable membrane (cf. § 16.14). In the case of a swollen piece of rubber there is no need for a membrane. The swollen, crosslinked rubber acts as its own membrane, as it were.

Since the vapors above the solvent and above the swollen piece of rubber my be considered to behave ideally, application of Raoult's Law (§ 16.12) leads to

$$\Pi \simeq -\frac{RT}{v_1} \ln P/P^{\circ} \, . \qquad (17.22)_2$$

At equilibrium swelling $P = P^{\circ}$ and thus $\Pi = 0$.

17.23 The Change in Free Enthalpy upon Swelling

Although we have defined the free enthalpy of dilution in § 17.21, we have said

The second term in Eq.(17.23)$_2$ is the free enthalpy change associated with the elastic isotropic expansion of the three-dimensional chain network upon swelling. As shown in continuum mechanics it is[14]

$$\Delta G_{\text{el}} = \tfrac{3}{2}\mathrm{G}(\lambda^2 - 1) \tag{17.23$_4$}$$

where $\lambda = 1/\bar{v}_2^{1/3}$ is the linear swelling ratio. Substituting for λ in the equation above gives

$$\Delta G_{\text{el}} = \tfrac{3}{2}\mathrm{R}T\nu_{\text{e}}(1/\bar{v}_2^{2/3} - 1) \tag{17.23$_5$}$$

where the relation $\mathrm{G} = \nu_e \mathrm{R}T$ [cf. Eq.17.17$_2$] serves to introduce the crosslink density, ν_{e}.

17.24 Swelling Equilibrium

Even when a piece of rubber is in contact with an *excess* of solvent, swelling eventually attains equilibrium when a balance is reached between the entropic forces promoting the mixing of the network chains and the solvent, and the elastic forces resisting the expansion of the network. At equilibrium, therefore, there can be no further penetration of solvent into the network. The condition for equilibrium, as already stated, is the vanishing of the free enthalpy of dilution, i.e., $\Delta G_1 = 0$. We thus have

$$\Delta G_1 = \frac{\partial \Delta G_{\text{sw}}}{\partial N_1} = \frac{\partial \Delta G_{\text{mix}}}{\partial N_1} + \frac{\partial \Delta G_{\text{el}}}{\partial N_1} = 0\,. \tag{17.24$_1$}$$

To take the derivative of the mixing term, we need to take into account that the volume fractions are given by Eqs.(16.17)$_2$ containing the number, x, of solvent-sized segments. Differentiation, and letting x increase without limit, i.e., letting $x \to \infty$, yields

$$\frac{\partial \Delta G_{\text{mix}}}{\partial N_1} = \mathrm{R}T[ln(1 - \bar{v}_2) + \bar{v}_2 + \chi\bar{v}_2^2]\,. \tag{17.24$_2$}$$

To differentiate the second term, consider that a unit cube of dry rubber will swell to a volume of $1 + N_1 v_1$, where v_1 is the molar volume of the solvent and $N_1 v_1$ is thus the volume of solvent that entered the cube. The volume fraction of the rubber in the swollen volume therefore becomes

$$\bar{v}_2 = \frac{1}{1 + N_1 v_1} \tag{17.24$_3$}$$

Substituting $1/\bar{v}_2 = 1 + N_1 v_1$ into Eq.(17.24) and differentiating leads to

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[14] Different theoretical considerations lead to different expressions for the front factor that is here given as 3/2. For details see Mark and Erman (1988).

$$\frac{\partial \Delta G_{el}}{\partial N_1} = RT\nu_e v_1 \bar{v}_2^{1/3} \,. \qquad (17.24)_4$$

Combining both equations and applying the equilibrium condition, $\Delta G_1 = 0$, yields

$$ln(1 - \bar{v}_2) + \bar{v}_2 + \chi\bar{v}_2^2 + \nu_e v_1 \bar{v}_2^{1/3} = 0 \,. \qquad (17.24)_5$$

This equation contains three 'unknowns': the equilibrium volume fraction v_2, the interaction parameter χ, and the crosslink density ν_e. Expanding the logarithm to the first two terms gives the equilibrium swelling volume as

$$\bar{v}_2 \simeq \left[\frac{0.5 - \chi}{v_1 \nu_e}\right]^{5/3} \,. \qquad (17.24)_6$$

Since χ may be taken as a constant less than 0.5 it is clear that the equilibrium swelling volume will be the smaller, the greater ν_e is.

Measurement of $\bar{v}_2$ provides one method for determining the crosslink density, ν_e, and/or the (number average) molecular mass, M_c, of the network chains from

$$\nu_e = \rho/M_c = -\frac{ln(1 - \bar{v}_2) + \bar{v}_2 + \chi\bar{v}_2^2}{v_1 \bar{v}_2^{1/3}} \qquad (17.24)_7$$

if the interaction parameter, χ, is known.

18. STABILITY

A thermodynamic system that returns to its original equilibrium state upon having been subjected to a perturbation is said to be in *stable equilibrium*. The present chapter examines the circumstances under which a system will act in this way. Under certain circumstances, however, a thermodynamic system may become *unstable*. The system then separates into distinct subsystems, called *phases*, thus exhibiting the phenomena of *phase transitions* and the existence of *critical states* and *critical points*. These phenomena will be discussed more fully in Chapter 19. This chapter first examines the general aspects of thermodynamic stability. It considers stability within an isolated single system or *intrinsic stability*, and stability between the subsystems of a composite system or *mutual stability*.

18.0 Chapter Contents

18.1 The Criteria of Thermodynamic Stability

The stability criteria, or criteria of stable equilibrium, are

$$(d^2U)_S > 0 \qquad \text{and} \qquad (d^2S)_U < 0 \tag{18.1$_1$}$$

based respectively on the energy minimum principle or the entropy maximum principle (cf. §§ 4.4 and 4.3). These criteria are valid for perturbations from a state of stable equilibrium. They are *sufficient* criteria, complementing the equilibrium criteria,

$$(dU)_S = 0 \qquad \text{and} \qquad (dS)_U = 0, \tag{18.1$_2$}$$

as *necessary* conditions. Our task now is to express the stability criteria in terms of quantities that are accessible experimentally. These will be the fundamental and the primary sets of second-order partial derivatives (cf. §§ 10.1 and 10.2) of the fundamental equation. We note that a valid fundamental equation must satisfy the criteria of stability.

18.2 Intrinsic Stability

We examine the problem of intrinsic stability, i.e., stability in an isolated system. Let

$$y^{(0)} = y^{(0)}(x_1, x_2, \dots x_n) \qquad (18.2)_1$$

denote either S or U with extensive parameters $x_1, x_2, \dots x_n$. and let us consider a general virtual displacement from equilibrium. The result of this perturbation will be given by the Taylor expansion

$$y^{(0)}(x_1 + dx_1, \dots x_n + dx_n) - y^{(0)}(x_1, \dots x_n) = dy^{(0)} + \frac{1}{2}\, d^2y^{(0)} + \dots \qquad (18.2)_2$$

The first-order effects form the series

$$dy^{(0)} = \sum_{i=1}^{n} y_i^{(0)}\, dx_i\,, \qquad (18.2)_3$$

and the second-order effects result as

$$d^2y^{(0)} = \sum_{i=1}^{n}\sum_{j=1}^{n} y_{ij}^{(0)}\, dx_i\, dx_j\,, \qquad (18.2)_4$$

where we have used the shorthand notation

$$y_{ij}^{(0)} = \left.\frac{\partial^2 y^{(0)}}{\partial x_i \partial x_j}\right|_{x_1, x_2, \dots x_{i-1}, x_{i+1}, \dots x_{j-1}, x_{j+1}, \dots} \qquad (18.2)_5$$

Now $dy^{(0)}$ is either $d(U)_S$ or $(dS)_U$ and the first-order effects therefore vanish by the conditions of equilibrium, $d(U)_S = 0$ and $(dS)_U = 0$. By Eqs.$(18.1)_1$, however, the second-order effects must be greater or less than 0, i.e., we must have

$$d^2y^{(0)} > 0 \qquad \text{and} \qquad d^2y^{(0)} < 0 \qquad (18.2)_6$$

depending on whether U or S is the base function. Effects of order higher than the second can be neglected at this point but will be addressed again later in § 18.16.

18.3 The Stability Criteria in Quadratic Form

Mathematically, $d^2y^{(0)}$ is a homogeneous quadratic form. Setting

$$y_{ij}^{(0)} = \mathrm{A}_{ij}\,, \qquad dx_i = \mathrm{q}_i\,, \tag*{(18.3)$_1$}$$

Eq.(18.2)$_4$ becomes

$$d^2y^{(0)} = \sum_{i=1}^{n}\sum_{j=1}^{n} y_{ij}^{(0)}\, dx_i\, dx_j \;= \mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q} \tag*{(18.3)$_2$}$$

where $\mathbf{A}$ is a symmetric matrix formed from the A_{ij}, i.e., from the second-order partial derivatives of the chosen base function, and $\mathbf{q}$ is a column vector composed of the dx_i, i.e., the infinitesimals of the extensive parameters of the system. The symbol $^{\mathrm{T}}$ denotes the transpose of the vector $\mathbf{q}$. Thus, $\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q}$ is the quadratic form in matrix notation.

Reformulating the stability criteria in the matrix notation yields

$$d^2y^{(0)} = \mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q} > 0 \qquad \text{and} \qquad d^2y^{(0)} = \mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q} < 0 \tag*{$_5$(18.3)$_3$}$$

for the criteria in the energy representation and the entropy representation, respectively.

18.4 Phase Separation

We now examine the conditions under which the system would become *unstable*, i.e., would separate into two *phases*. Phases are homogeneous subsystems bounded by a surface across which the physical properties change discontinuously. As shown in Fig. 18.4 below, we imagine the system to be subdivided into two such phases which are initially identical, and are separated by a diathermal, movable, and permeable wall. This purely imaginary subdivision turns our single system effectively into a composite one. Indeed, we shall see later that the problem of intrinsic stability underlies the problem of mutual stability (cf. § 18.17).

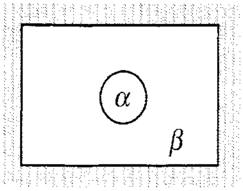

Fig. 18.4 Isolated system comprising two subsystems, α and β

We shall call the two subsystems the α-phase and the β-phase, respectively. The same Greek letters will be used as superscripts to distinguish quantities as belonging to one or the other phase. The perturbation effects for the composite system then are

$$d^2y^{(0)} = (\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q})^{\alpha} + (\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q})^{\beta}\,. \qquad (18.4)_1$$

In the Taylor expansion the partial derivatives are evaluated at the initial conditions and, by assumption, the α- and the β-phase are identical at the onset of the perturbation. Hence, introducing molar quantities, we find that

$$y_{ij}^{(0)\alpha} = \frac{N^{\alpha}}{N^{\beta}}\, y_{ij}^{(0)\beta}\,. \qquad (18.4)_2$$

The system being isolated, the conservation constraints, Eqs.$(4.6)_{1.1}$ or $(4.7)_1$, require that

$$dx_i^{\alpha}dx_j^{\alpha} = (\,-\,dx_i^{\beta})(\,-\,dx_j^{\beta}) = dx_i^{\beta}dx_j^{\beta}\,. \qquad (18.4)_3$$

Substituting Eqs. $(18.4)_2$ and $(18.4)_3$ into Eq.$(18.4)_1$ yields

$$d^2y^{(0)} = \frac{N}{N^{\beta}}\,(\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q})^{\alpha} \qquad (18.4)_4$$

where $N = N^{\alpha} + N^{\beta}$.

Equation $(18.4)_4$ contains derivatives (i.e., variations) only of the α-phase. The stability of the α-phase thus implies the stability of the β-phase. To examine the circumstances under which the phases would separate it is therefore sufficient to ascertain the criterion of stability for the α-phase alone.

18.5 Positive Definiteness of the Quadratic Form

The quadratic form can be arranged in the form of a square array. The $dx_j dx_j$-terms on the principal diagonal of the array, being squares, are necessarily positive. Nothing can be said, however, about the signs of the off-diagonal terms. To establish the conditions under which the form will be either positive or negative definite, it is therefore necessary to 'diagonalize' it, that is, to express it as a sum which contains no 'mixed' terms. One way of doing this is described in Appendix 6. The result is

$$\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q} = \sum_{j=1}^{n-1} y_{jj}^{(j-1)}\, d\mathrm{r}_j^2 \qquad (18.5)$$

where the $y_{jj}^{(j-1)}$ are the second-order partial derivatives of the Legendre transforms of order j–1 of the chosen base function. The identical subscripts mean that the stability criteria are based on second-order derivatives formed from conjugate pairs of parameters. No criteria can be based on any mixed partial derivative.

18.6 Criteria of Intrinsic Stability

Since dr_j^2 is necessarily positive, $\mathbf{q}^T\mathbf{A}\,\mathbf{q}$ will be positive or negative definite according to whether

$$y_{jj}^{(j-1)} > 0 \qquad \text{or} \qquad y_{jj}^{(j-1)} < 0\,. \qquad j = 1, 2, \ldots \mathrm{n}-1 \qquad (18.6)$$

Here, n = f + 1, n and f being the number of canonical variables and of degrees freedom.

The two inequalities above furnish the criteria of intrinsic stability. With U as the base function the method described in Appendix 6 leads to the first inequality while the choice of S as the base function leads to the second inequality instead.

18.7 Le Châtelier's Principle

The physical content of the two criteria embodied in the Inequalities (18.6) is known as Le Châtelier's principle. It states:

> *"Spontaneous processes induced by a displacement from equilibrium work to restore the system to equilibrium."*

As an example, suppose that in a portion of a system the temperature is raised above that of the rest of the system. The spontaneous process which will occur then is a flow of heat away from the hotter region (cf. § 4.10) until equilibrium is reestablished throughout the system.

Le Châtelier's principle carries the concept of equilibrium from mechanics to thermodynamics. It applies not only to physical processes such as phase changes but to chemical reactions as well (cf.. § 21.8).

18.8 Stability Criteria in the Simple System - Energy Representation

In this section we demonstrate the method for formulating the stability criteria in the internal energy representation, based on the first inequality of § 18.6.

$$y_{jj}^{(j-1)} > 0$$

In § 18.14 we give a brief illustration using the entropy representation.

Consider a binary simple system that has $U = (S, V, N_{\mathrm{A}}, N_{\mathrm{B}})$ for its fundamental equation. The system is characterized by four extensive parameters, hence there will be three criteria, to be derived from the second-order partial derivatives of the fundamental equation's Legendre transforms of zeroth, first, and second-order. Since the two mole fractions are interrelated by the appropriate form of the Gibbs-Duhem equation (cf. § 14.14), the mole number of any one of the components is sufficient to characterize the system. We have arbitrarily chosen N_A.

In the 'standard' order, $y^{(0)} = U(S, V, N_\mathrm{A})$, the transforms and their canonical variables[15] are

$$y^{(0)} = U(S, V, N_\mathrm{A}),$$

$$y^{(1)} = F(T, V, N_\mathrm{A}),$$

and

$$y^{(2)} = G(T, -P, N_\mathrm{A}).$$

Writing A for N_A for notational simplicity, the second-order partial derivatives take the forms:

$$y_{11}^{(0)} = \frac{\partial^2 U}{\partial S^2} = U_{SS}\ ,$$

$$y_{22}^{(1)} = \frac{\partial^2 F}{\partial V^2} = F_{VV},$$

and

$$y_{33}^{(2)} = \frac{\partial^2 G}{\partial \mathrm{A}^2} = G_\mathrm{AA}\ .$$

We have made use here of the handy 'double subscript' notation for the second order partial derivatives. With this notation we obtain succinctly

$$U_{SS} > 0\ , \qquad (18.8)_1$$

$$F_{VV} > 0\ , \qquad (18.8)_2$$

and

$$G_\mathrm{AA} > 0\ . \qquad (18.8)_3$$

for the three criteria of a binary simple system.

18.9 The Criterion of Thermal Stability

Since

$$U_{SS} = (\partial T/\partial S)_{V,N_\mathrm{A},N_\mathrm{B}} = T/C_V \qquad (18.9)_1$$

---

[15] The pressure is best handled as $-P$, adjusting the notation eventually as appropriate.

[cf. Eq.(10.1)$_1$], we have $T/C_V > 0$. But this can be true only if

$$C_V > 0\,. \tag{18.9$_2$}$$

The criterion is appropriately called the criterion of *thermal stability* because the intensive variable to which it relates is the temperature. Since, at constant volume and mole numbers, $T\mathrm{d}S = \delta\mathrm{Q}$, we have $\delta\mathrm{Q}/dT > 0$. The criterion, therefore, states the rather obvious fact that the addition of heat to a stable system increases its temperature.

18.10 The Criterion of Mechanical Stability

Next,

$$F_{VV} = -(\partial P/\partial V)_{T,N_\mathrm{A},N_\mathrm{B}} = 1/V\kappa_T \tag{18.10$_1$}$$

[cf. Eq.(10.2)$_3$], and the second criterion becomes

$$\kappa_T > 0\,. \tag{18.10$_2$}$$

It implies that $\partial P/\partial V < 0$ and, hence, indicates that an isothermal expansion of a stable system at constant temperature must decrease its pressure. It is called the criterion of *mechanical stability*.

18.11 The Criterion of Diffusional Stability

Finally,

$$G_\mathrm{AA} = (\partial\mu/\partial N_\mathrm{A})_{T,P,N_\mathrm{B}}\,. \tag{18.11$_1$}$$

No special symbol for the derivative is in common use. Introducing the mole fraction, $\overline{n}_\mathrm{A}$, we obtain the third criterion in the form

$$\partial\mu_\mathrm{A}/\partial\overline{n}_\mathrm{A} > 0\,. \tag{18.11$_2$}$$

This may be referred to as the criterion of *diffusional stability* because it expresses the fact that the introduction of an additional amount of matter into a stable system at constant temperature and pressure will increase its chemical potential.

18.12 Effect of Parameter Ordering

The criteria listed in the preceding section were obtained by taking the extensive parameters of the base function in the 'standard' ordering $y^{(0)} = U(S, V, N_\mathrm{A}, N_\mathrm{B})$. A different ordering produces different but equivalent criteria. We illustrate this again for the binary simple system. The ordering $U = U(V, S, N_\mathrm{A}, N_\mathrm{B})$, for example, will furnish the relations

$$y^{(0)} = U(V, S, N_{\mathrm{A}}),$$

$$y^{(1)} = H(-P, S, N_{\mathrm{A}}),$$

and

$$y^{(2)} = G(-P, T, N_{\mathrm{A}}).$$

The second-order partial derivatives then follow as

$$y_{11}^{(0)} = \frac{\partial^2 U}{\partial \mathrm{S}^2} = U_{VV}$$

$$y_{22}^{(1)} = \frac{\partial^2 U}{\partial \mathrm{S}^2} = H_{SS}$$

and

$$y_{33}^{(2)} = \frac{\partial^2 U}{\partial \mathrm{A}^2} = G_{\mathrm{AA}}$$

The second-order transform remained as it was in § 18.8 since the position of N_{A} was not changed in the new ordering. The two new criteria now become

$$U_{VV} > 0\,, \tag{18.12$_1$}$$

and

$$H_{SS} > 0\,. \tag{18.12$_2$}$$

But

$$U_{VV} = -(\partial P/\partial V)_{S,N_{\mathrm{A}},N_{\mathrm{B}}} = 1/V\kappa_S \tag{18.12$_3$}$$

[cf. Eq.(10.1)$_3$] and, hence,

$$\kappa_S > 0\,. \tag{18.12$_4$}$$

This is another form of the criterion of mechanical stability. It implies that an isentropic expansion of a stable system increases its temperature as does an isothermal expansion.

Now

$$H_{SS} = (\partial T/\partial S)_{P,N_{\mathrm{A}},N_{\mathrm{B}}} = T/C_P \tag{18.12$_5$}$$

[cf. Eq.$(10.2)_1$] which, in turn, gives

$$C_P > 0 \,, \qquad (18.12)_6$$

Equation $(10.3)_3$, $C_P = C_V + TV\alpha_P^2/\kappa_T$, shows that $C_P > 0$ implies $C_V > 0$ because $TV\alpha_P^2/\kappa_T > 0$ if $\kappa_T > 0$. Further, it is readily seen from $\kappa_T/\kappa_S = C_P/C_V$ that $\kappa_S > 0$ implies $\kappa_T > 0$ because C_P is always greater than C_V. Clearly, the two sets of criteria obtained from the two different orderings are equivalent although they differ in form.

18.13 Sufficiency of the Highest-Order Criterion

The highest order criterion ($j = n - 1 = \mathrm{f}$) is a *sufficient* criterion. The lower order ones are *necessary*, but not sufficient criteria. Consider the two criteria of the single component simple system,

$$U_{SS} > 0 \,, \qquad (18.13)_1$$

and

$$F_{VV} = (U_{SS}\, U_{VV} - U_{SV}^2) > 0 \,. \qquad (18.13)_2$$

Now let U_{SS} decrease. Then, F_{VV} will become negative *before* U_{SS} can become zero (or negative), unless U_{VV} increases without limit. Thus, the second criterion is violated before the first.

This reasoning can be extended to systems with an arbitrary number of extensive parameters. In general, the necessary *and* sufficient criterion for a stable equilibrium is

$$y_{(n-1)(n-1)}^{(n-2)} = y_{\mathrm{ff}}^{(\mathrm{f}-1)} > 0 \qquad \text{or} \qquad y_{(n-1)(n-1)}^{(n-2)} = y_{\mathrm{ff}}^{(\mathrm{f}-1)} < 0 \,, \qquad (18.13)_3$$

depending on whether the criterion is sought in the energy, or in the entropy representation. The equations above are, of course, the Inequalities 18.6 with $\mathrm{f} = j$.

18.14 Stability Criteria in the Simple System - Entropy Representation

The last three sections dealt with formulating the stability criteria based on the internal energy representation. An analogous procedure based on the second of the inequalities of § 18.6,

$$y_{jj}^{(j-1)} < 0 \,,$$

furnishes the stability criteria in the entropy representation. This approach makes use of Ψ and Φ, two of the Massieu functions introduced in Chapter 9. We shall obtain here the criteria for the binary simple system we have used in § 8.8. For this system

$$y^{(0)} = S(U, V, N_\mathrm{A}) ,$$

$$y^{(1)} = \Psi(1/T, V, N_\mathrm{A}) ,$$

and

$$y^{(2)} = \Phi(1/T, 1/P, N_\mathrm{A}) ,$$

where Ψ, THE Massieu function, is given by Eq.(9.1)$_2$, while Φ, the Planck function, is given by Eq.(9.2)$_1$.

Again using A for N_A, the derivatives become

$$y_{11}^{(0)} = \frac{\partial^2 S}{\partial U^2} = S_{UU}$$

$$y_{22}^{(1)} = \frac{\partial^2 \Psi}{\partial V^2} = \Psi_{VV}$$

and

$$y_{33}^{(2)} = \frac{\partial^2 \Phi}{\partial \mathrm{A}^2} = \Phi_{\mathrm{AA}} .$$

The three criteria require that we have

$$S_{UU} < 0 \tag{18.14$_1$}$$

$$\Psi_{VV} < 0 \tag{18.14$_2$}$$

and

$$\Phi_{\mathrm{AA}} < 0 . \tag{18.14$_3$}$$

Now,

$$S_{UU} = \left.\frac{\partial^2 S}{\partial U^2}\right|_{V,\mathrm{A}} = \left.\frac{\partial (1/T)}{\partial U}\right|_{V,\mathrm{A}} = \left.\frac{\partial 1/T}{\partial T}\frac{\partial T}{\partial U}\right|_{V,\mathrm{A}} = -\frac{1}{T^2 C_V} , \tag{18.14$_4$}$$

since $(\partial U/\partial T)_V = C_V$ by Eq.(10.1)$_4$. But then the criterion $S_{UU} < 0$ can only be true if $C_V > 0$ and thus we recover the criterion of thermal stability.

Similarly,

$$\Psi_{VV} = \left.\frac{\partial^2 \Psi}{\partial V^2}\right|_{T,\mathrm{A}} = \left.\frac{\partial (P/T)}{\partial V}\right|_{T,\mathrm{A}} = \left.\frac{1}{T}\frac{\partial P}{\partial V}\right|_{T} = -1/\kappa_T V . \tag{18.14$_5$}$$

But then the criterion $\Psi_{VV} < 0$ can only be true if $\kappa_T > 0$, and this is the criterion of mechanical stability that we had found earlier.

Finally,

$$\Phi_{\mathrm{AA}} = \left.\frac{\partial^2\Phi}{\partial A^2}\right|_{T,P} = -\left.\frac{\partial(\mu/T)}{\partial A}\right|_{T,P} = -\left.\frac{1}{T}\frac{\partial\mu}{\partial A}\right|_{T,P} = -\,\partial\mu_{\mathrm{A}}/T\partial\bar{n}_{\mathrm{A}} \qquad (18.14)_6$$

which is another expression for the criterion of *diffusional stability* of § 18.11.

18.15 Critical States

At the limit of intrinsic stability the Inequalities (18.6) become the equality

$$y_{jj}^{(j-1)} = 0\,, \qquad j = 1,2,\ldots n-1 \qquad (18.15)$$

in either representation.

A system at the limit of stability is in a *critical state* since it can become unstable by an infinitesimal variation in conditions. Not all phase transitions have critical states.

18.16 Critical Points

Critical states are characterized by *critical points*. To decide whether a perturbation will take the system into a stable or an unstable state, we must examine perturbations of order higher than the second in the Taylor expansion, Eq.(18.2)$_2$. Given n canonical variables, we must therefore look at

$$dy_{jj}^{(j-1)} = y_{jjj}^{(j-1)}\,dx_j\,. \qquad j = 1,2,\ldots n-1 \qquad (18.16)_1$$

Let us assume that the α-phase is stable and that

$$y_{jj}^{(j-1)\alpha} > 0\,. \qquad j = 1,2,\ldots n-1 \qquad (18.16)_2$$

Then, Eq.(18.16)$_1$ becomes

$$dy_{jj}^{(j-1)\alpha} = y_{jjj}^{(j-1)\alpha}\,dx_j^{\alpha} > 0\,. \qquad j = 1,2,\ldots n-1 \qquad (18.16)_3$$

Since the system is isolated we have $dx_j^{\alpha} + dx_j^{\beta} = 0$. Hence, whatever the sign of dx_j^{α}, that of dx_j^{β} is its negative inverse. If $dx_j\alpha > 0$ it would follow that

$$dy_{jj}^{(j-1)\beta} = y_{jjj}^{(j-1)\beta}\, dx_j^{\beta} < 0\,. \qquad j = 1, 2, \ldots n-1 \qquad (18.16)_4$$

Equations $(18.16)_3$ and $(18.16)_4$ are in contradiction with the original assumption that the α- and β-phase are identical before the onset of the perturbation. Therefore, we must set

$$y_{jjj}^{(j-1)} = 0\,. \qquad j = 1, 2, \ldots n-1 \qquad (18.16)_5$$

This, together with the conditions

$$y_{jjjj}^{(j-1)} > 0 \qquad \text{or} \qquad y_{jjjj}^{(j-1)} < 0\,, \qquad j = 1, 2, \ldots n-1 \qquad (18.16)_6$$

is the criterion for the existence of a stable *critical point*. The first condition applies in the energy, and the second in the entropy representation. An application of these equations is discussed in § 19.10.

If the fourth order derivative is found to vanish, the fifth order derivative must be zero for a stable critical point to exist. In general, if the internal energy is selected as the base function, the lowest non-vanishing derivative of even order must be positive for that critical point to be stable.

18.17 Mutual Stability

The stability of the mutual equilibrium state of two single component simple systems interacting through a non-restrictive wall is guaranteed by the intrinsic stability of the individual systems. Intrinsic stability thus dominates the problem of mutual stability.

19. PHASE TRANSITIONS

If the criteria of intrinsic stability are not satisfied, the system breaks up into one or more portions or *phases*. Examples are common. The phases of water have been studied extensively from the beginning of thermodynamic investigations, largely because of the role of water as the working fluid in steam engines that utilize the liquid-vapor transition of water to produce useful work. Water is also a common solvent.

19.0 Chapter Contents

19.1 Phase Transitions in an Ideal Gas

An ideal gas is by definition in stable equilibrium because the stability criteria are intrinsically satisfied for all ideal gases. The criterion of thermal stability, $C_V > 0$, is satisfied because for all ideal gases, the heat capacities are always positive [cf. Eq.$(12.5)_3$]. Similarly, so is the criterion of mechanical stability, $\kappa_T > 0$ [cf. Eq.$(12.5)_2$]. An ideal gas, therefore, does not exhibit the phenomena of phase transitions and critical points.

19.2 The van der Waals Equation of State

To illustrate the theoretical aspects of the liquid-vapor (or liquid-gas) transition in water and other fluids we turn to the semi-empirical *van der Waals equation of state* (van der Waals 1873). This equation is an extension of the second equation of state of the ideal gas. It models the behavior of real gases at moderately low temperatures and moderately high pressures quite well. For the physical simple system the equation takes the form

$$(P + a/v^2)(v - b) = RT \qquad (19.2)_1$$

where a and b are material constants.

Figure 19.1 shows a schematic plot of the pressure, P, against the molar volume, v, at different temperatures, T, for an arbitrary set of the constants, a and b.

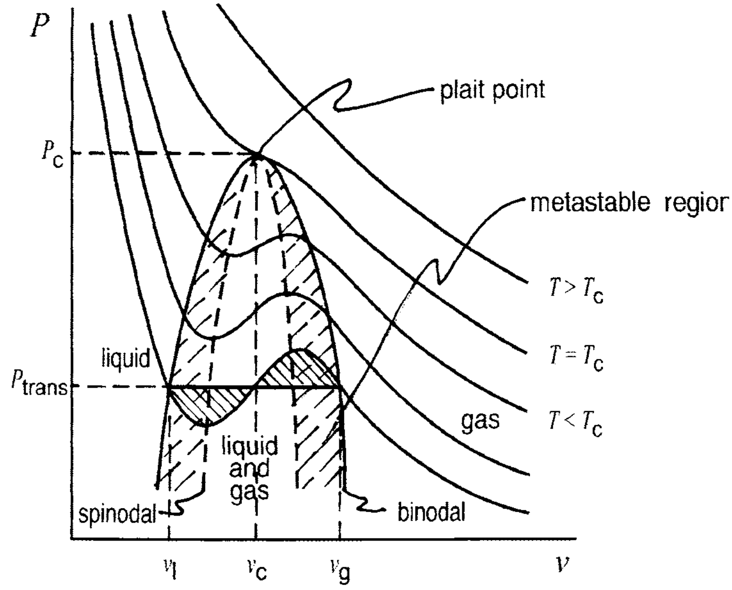

Fig. 19.2 Van der Waals isotherms

By Eq.(10.2)$_3$ the slope, $(\partial P/\partial v)_T$, of the isotherms must obey the relation

$$\left.\frac{\partial P}{\partial v}\right|_T = -1/v\kappa_T\,. \qquad (19.2)_2$$

Since the physical simple system has two degrees of freedom, by Eq.(18.13)$_{3.1}$ the highest order stability criterion becomes

$$y_{22}^{(1)} = F_{vv} = -\left.\frac{\partial P}{\partial v}\right|_T > 0 \qquad (19.2)_3$$

But this is the criterion of mechanical stability, $\kappa_T > 0$ (§ 18.10). The criterion is fulfilled everywhere along these isotherms at higher temperatures where the slope is everywhere negative. At these temperatures the system is therefore in stable equilibrium and will not separate into phases. The fluid can only exist as a vapor, i.e., a gas, and the gas cannot be liquefied at any pressure. At lower temperatures the slope changes sign, the system becomes unstable, and phase separation can occur. Liquid and vapor can then coexist.

19.3 The Critical Point

The lowest of the stable isotherms is called the *critical isotherm*. It contains a horizontal point of inflection at which

$$\left.\frac{\partial P}{\partial v}\right|_T = \left.\frac{\partial^2 P}{\partial v^2}\right|_T = 0\,. \tag{19.3$_1$}$$

By Eq.(18.15) the criterion for a critical state becomes

$$y_{22}^{(1)} = F_{vv} = \left.\frac{\partial^2 F}{\partial v^2}\right|_T = -\left.\frac{\partial P}{\partial v}\right|_T = 0\,. \tag{19.3$_2$}$$

The inflection point in the critical isotherm is therefore the *critical point* or *plait point* (cf. § 18.16). The pressure, volume, and temperature at the critical point are the *critical pressure*, P_c, the *critical (molar) volume*, v_c, and the *critical temperature*, T_c.

19.4 The Spinodal

Below the critical isotherm, the constant temperature van der Waals curves develop minima and maxima. These denote the limits of intrinsic stability at which Eq.(18.15) becomes

$$\left.\frac{\partial P}{\partial v}\right|_T = 0\,. \tag{19.4}$$

The parabola-like spike shown as a dashed line in Fig. 19.2 is called the *spinodal*. It passes through the minima on the left up to the critical point and then down through the maxima on the right, demarcating the *region of absolute instability*. The slope of the van der Waals isotherm is positive within this region, thus violating the criterion of mechanical stability. Consequently, within it part of the fluid must exist as a vapor (i.e., gas), the other part must exist as a liquid.

19.5 The Binodal - Maxwell's Rule

Liquid and vapor can also coexist, however, outside the region demarcated by the spinodal. The region of incipient phase separation is marked off by the *binodal* shown in Fig. 19.2 as the solid parabola-like curve. The binodal marks the endpoints of the horizontal portion of the true isotherm. This is the horizontal line marked $P = P_{\text{trans}}$, where P_{trans} is the pressure that remains constant during the phase transition. The line is drawn in such a way that the areas enclosed by it and by the isotherm below and above it have equal areas as shown in Fig. 19.2. This construction is due to Maxwell and is known as *Maxwell's rule* or *Maxwell's construction.*

19.6 The Metastable Region

At the endpoint of the line, i.e., at the binodal points, $(\partial P/\partial v)_T < 0$, and the system is in stable equilibrium. Inside the binodal, however, in the region between the binodal and the spinodal, the system is in *metastable equilibrium*. With careful supercooling or superheating it is possible to proceed along the van der Waals isotherm towards the points of absolute instability represented by the spinodal. Normally, however, the system will follow along the horizontal part of the isotherm given by Maxwell's construction. Thus, the region between the binodal and the spinodal is a *region of metastable equilibrium.*

19.7 The Saturation region

When a gas is compressed isothermally below the critical temperature, T_c, its pressure first rises slowly because the gas is highly compressible. When the isotherm attains the binodal, saturation occurs, i.e., the vapor begins to condense. The pressure now stays constant until the left branch of the binodal is reached, at which point the pressure rises more steeply because the liquid is relatively incompressible. If the left branch is approached from the left, at the binodal it is now the liquid which is saturated and it begins to vaporize. Hence, the region within the binodal, including the region within the spinodal, is also known as the *saturation region.*

19.8 The Lever Rule

Within the saturation region an arbitrary fraction of the fluid is present as a liquid in equilibrium with the vapor. The state of the system may be characterized by the average molar volume,

$$v_{\text{av}} = \overline{n}_\ell \, v_\ell + \overline{n}_{\text{g}} \, v_{\text{g}} \,, \tag{19.8$_1$}$$

of the total system, where $v_\ell < v_{\text{av}} < v_{\text{g}}$, and v_ℓ and v_{g} are the (molar) volumes at the left (i.e., the liquid) and the right (i.e., the gas) endpoints of the horizontal part of the isotherm (cf. Fig. 19.2). The volume v_{av} divides this horizontal part of the isotherm in the ratio of the mole fractions of the fluid in the gas phase, $\overline{n}_{\text{g}}$, to that in the liquid phase, $\overline{n}_\ell$. But $\overline{n}_\ell + \overline{n}_{\text{g}} = 1$ and, therefore,

$$(\overline{n}_\ell + \overline{n}_{\text{g}}) \, v_{\text{av}} = \overline{n}_\ell \, v_\ell + \overline{n}_{\text{g}} \, v_{\text{g}} \,. \tag{19.8$_2$}$$

Rearranging gives

$$\frac{\overline{n}_{\text{g}}}{\overline{n}_\ell} = \frac{v_{\text{av}} - v_\ell}{v_{\text{g}} - v_{\text{av}}} . \tag{19.8$_3$}$$

Now let d_ℓ be the distance $(v_{\mathrm{av}} - v_\ell)$ between the liquid endpoint and the point of division, and d_{g} the distance $(v_{\mathrm{g}} - v_{\mathrm{av}})$ between the division point and the gas endpoint in Fig. 19.2. Then Eq.(19.8)$_3$ becomes

$$\overline{n}_\ell\,\mathrm{d}_\ell = \overline{n}_{\mathrm{g}}\,\mathrm{d}_{\mathrm{g}}\,. \tag{19.8$_4$}$$

This expression is known as the *lever rule* because it is a formal analog of the rule for the mechanical equilibrium of forces around a fulcrum at the division point with weights equal to the mole fractions $\overline{n}_\ell$ and $\overline{n}_{\mathrm{g}}$ at the liquid and gas endpoints, respectively.

Subtracting v_ℓ from both sides of Eq.(19.8)$_1$ and using $\overline{n}_\ell + \overline{n}_{\mathrm{g}} = 1$ gives

$$v_{\mathrm{av}} - v_\ell = \overline{n}_{\mathrm{g}}(v_{\mathrm{g}} - v_\ell) \tag{19.8$_5$}$$

from which it follows that

$$\overline{n}_{\mathrm{g}} = \frac{\mathrm{d}_\ell}{\mathrm{d}_\ell + \mathrm{d}_{\mathrm{g}}}\,. \tag{19.8$_6$}$$

By an analogous derivation then

$$\overline{n}_\ell = \frac{\mathrm{d}_{\mathrm{g}}}{\mathrm{d}_\ell + \mathrm{d}_{\mathrm{g}}}\,. \tag{19.8$_7$}$$

These two equations allow us to find the mole fractions of the gas and the liquid for any point along the flat portion of the isotherm.

19.9 Phase Equilibrium and Stability Criteria in Terms of the Free Energy

Since we are considering changes along isotherms, it is instructive to view these changes in the light of the equilibrium and stability criteria expressed in terms of the free energy, F. The equilibrium criterion is

$$(dF)_T = 0. \tag{19.9$_1$}$$

In § 8.12 we introduced the stability criterion for perturbation from a state of stable equilibrium as $(d^2F)_T > 0$. However, at the limit of stability $(d^2F)_T$ vanishes. In accordance with § 18.16, we must therefore examine higher order perturbations as well, and the criteria of stability become

$$(d^2F)_T \geq 0 \qquad \text{and} \qquad (d^nF)_T > 0 \tag{19.9$_2$}$$

where $(d^n F)_T$ is the lowest-order non-vanishing variation. We proceed to examine this case.

19.10 The F, v–Diagram

Let us consider F as a function of v. An F, v–diagram is shown in Fig. 19.10 for the physical simple system. The points A and B represent points on that isotherm. They have a common tangent of slope $(\partial F/\partial v)_T = -P$. The two points C and D are the spinodal points, at which $(\partial P/\partial v)_T = 0$. They represent the minima and maxima in the van der Waals isotherm. By § 18.15 both points therefore indicate a critical state[16]. Since

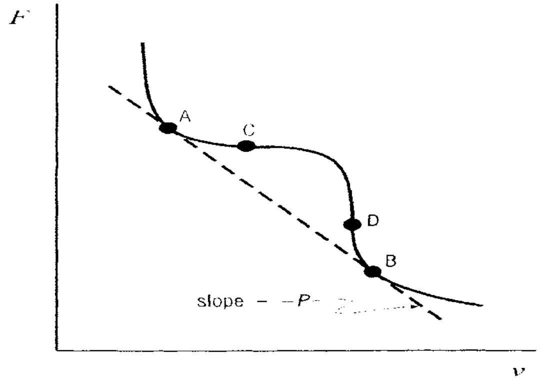

Fig. 19.10 F, v – diagram for the physical simple system

$$(d^2F)_T = -\left.\frac{\partial P}{\partial v}\right|_T (dv)^2_T = 0\,, \tag{19.10$_1$}$$

we must consider the variation of order three, i.e.,

$$(d^3F)_T = -\left.\frac{\partial^2 P}{\partial v^2}\right|_T (dv)^3_T\,, \tag{19.10$_2$}$$

in accordance with § 18.16.

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[16] Observe that we have

$$y^{(j-1)}_{jj} = y^{(1)}_{22} = F_{vv} = \frac{(\partial^2 F)_T}{(\partial v)^2_T} = \left.\frac{\partial^2 F}{\partial v^2}\right|_T$$

Now, the point **C** is a minimum in the $P,v-$diagram of Fig. 19.2. Consequently, $(\partial P/\partial v)_T$ is positive. Hence, for variations that *decrease* volume, i.e., for variations for which $(dv)_T^3 < 0$, $(d^3F)_T > 0$ and the phase is intrinsically stable. Conversely, for variations that *increase* volume, i.e., for variations for which $(dv)_T^3 > 0$, $(d^3F)_T < 0$ and the phase is unstable.

By contrast, the point **D** represents a maximum in Fig. 19.2. Hence, here $(\partial P/\partial v)_T$ is negative, and the phase is stable for variations that increase volume, and unstable otherwise. The two considerations bear out the contention that points along the spinodal represent critical states.

We note that between the points **C** and **D** the derivative $(\partial P/\partial v)_T$ is always positive. Hence, by Eq.(19.10)$_1$, $(dF)_T^2$ is then negative and the system is always unstable. Between the points **A** and **C**, and between **D** and **B** the system is stable for some changes and unstable for others. Hence, it is metastable.

As the temperature is increased to the critical temperature, T_c, the two spinodal points coalesce in the critical point. At this unique point, again in accordance with § 18.16,

$$(dF)_T = (d^2F)_T = (d^3F)_T = 0\,, \qquad (d^4F)_T \geq 0\,, \tag{19.10$_3$}$$

i.e.,

$$\left.\frac{\partial P}{\partial v}\right|_T = \left.\frac{\partial^2 P}{\partial v^2}\right|_T = \left.\frac{\partial^3 P}{\partial v^3}\right|_T = 0\,, \qquad \left.\frac{\partial^4 P}{\partial v^4}\right|_T \geq 0. \tag{19.10$_4$}$$

The latter is therefore the lowest non-vanishing variation.

Above the critical point, $(\partial P/\partial v)_T$ is always negative, and the system is always stable.

19.11 Latent Heat

We have discussed liquid-vapor transitions (condensation/evaporation) in the physical simple system. Similar considerations apply, however, to other phase transitions such as the solid-liquid transition (crystallization/fusion), the solid-vapor transition (crystallization/sublimation), or solid-solid transitions between different crystalline forms of the same substance.

A phase transition necessarily entails a change in entropy. At constant temperature the change in molar entropy, Δs, is associated with the heat flux, $T\Delta s = Q$, between the system and the heat reservoir which keeps the temperature constant. This heat flux is called the *latent heat*, Λ, which therefore represents the *heat of vaporization, fusion, crystallization, sublimation,* etc., as the case may be.

19.12 The Clapeyron Equation – Phase Equilibrium

By the equilibrium condition, Eq.(4.6)$_3$, the chemical potentials of two coexisting phases must be equal. For the physical simple system we must therefore have

$$\mu^\alpha(T,P) = \mu^\beta(T,P)\,, \tag{19.12$_1$}$$

where the superscripts α and β denote the two phases, respectively. This implies a functional relation between the temperature, T, and the pressure, P, of the system. We proceed to make this relation explicit.

By the Gibbs-Duhem equation for the physical simple system we have

$$d\mu^{\alpha} = -s^{\alpha}dT + v^{\alpha}dP \tag{19.12$_2$}$$

and

$$d\mu^{\beta} = -s^{\beta}dT + v^{\beta}dP\,. \tag{19.12$_3$}$$

Thus the chemical potentials of the two phases can be represented by two surfaces above the P, T-plane.

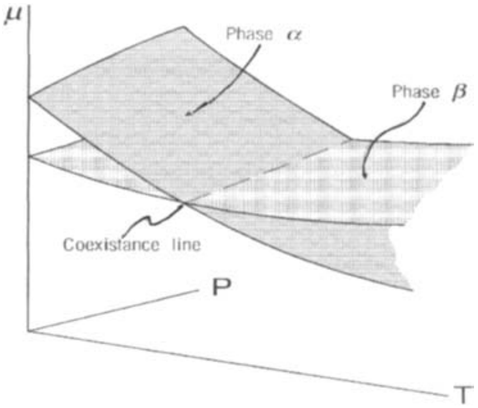

Fig. 19.12 Chemical potential surfaces for two phases, α and β

The projection of their intersection forms a line in the plane, the *coexistence line*. In the case of liquid-vapor equilibrium, the coexistence line is the vaporization curve which ends in the critical point (T_c, P_c) as displayed in Fig. 19.15 below.

By Eq.(19.12)$_1$ we then obtain

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta S}{\Delta V}\,, \tag{19.12$_4$}$$

an equation first derived by Clapeyron.

19.13 The Clausius-Clapeyron Equation

Let us further elaborate the Clapeyron equation. To express the right-hand side of Eq.(19.12)$_4$ in terms of measurable quantities, we introduce the Clausius equality, Eq.(5.2), in the form $\Delta S = Q/T$. But now the heat, Q, is the latent heat, Λ, and at constant pressure this is equal to the change in the enthalpy, ΔH, in accordance with Eq.$(8.7)_3$. Hence, we obtain the equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}\,. \qquad (19.13)_1$$

Because it was derived for a single-component simple system, this equation is valid in this form only as long as the chemical potentials do not depend on the composition.

When one of the phases is a condensed phase (a liquid or a solid), and the vapor above the phase can be considered to be ideal, the approximation $\Delta V = V^{\text{vap}} = \mathrm{R}T/P$ furnishes the Clausius-Clapeyron equation in the form

$$\frac{d\,ln\,P}{dT} = \frac{\Lambda}{\mathrm{R}T^2}\,. \qquad (19.13)_2$$

This is valid only as long as P is not too large.

19.14 The Triple Point

If we had three instead of two phases in equilibrium, the condition of equilibrium between the chemical potentials, i.e., the conditions of phase equilibrium, would be

$$\mu^\alpha(T,P) = \mu^\beta(T,P) = \mu^\gamma(T,P)\,. \qquad (19.14)$$

Since we now have two equations in the two variables, T, and P, the solution gives the coordinates of a point in the $P,T-$plane. This point is called the *triple point.* A pure substance may have several triple points since it may exist in several forms in the solid state. Nevertheless, the maximum number of coexisting phases of a pure substance is three. This is expressed by the phase rule that forms the subject of § 19.16. A well-known example is the triple point of water at which solid, liquid, and vapor phases coexist. Taking the temperature of this point to be 273.16 K defines the absolute thermodynamic temperature scale (cf. § 7.14).

19.15 Coexistence Lines and Existence Regions

The $P,T-$plane of a typical pure substance is shown in Fig. 19.15. We distinguish three regions in the $P,T-$plane below the critical temperature: the solid, liquid, and gas (or vapor) regions. They are separated by the *coexistence lines*, here the *fusion* or *melting-point curve*, the *sublimation curve*, and the *vaporization* or *vapor-pressure curve*, respectively. The three lines meet in the triple point. While the fusion curve extends upward indefinitely, the vaporization curve ends in the *critical point* C.

In each of the three regions the substance must be entirely in the respective phase. To see this more clearly, consider that the dashed portion of the vaporization curve, the coexistence line for the gas and the liquid, lies above the chemical potential surface for the solid. For the free energy to be a minimum in this region, the substance must therefore be entirely in the solid phase. This, then, is the only stable phase in this region. Consequently, it is known as the *existence region* of the solid phase. Similar considerations apply to the other two existence regions.

The critical point marks the highest temperature and pressure at which a pure substance can exist in liquid-vapor equilibrium. At higher temperatures and pressures the material exists in the fluid (or supercritical) region. The dashed lines emanating from the critical point indicate the boundaries of this region. There are no phase transitions across these boundaries. Indeed, it is possible to proceed from the liquid to the gas phase without any visible phase transition by circum-navigating the critical point as indicated by the curved arrow connecting points *A* and *B* in Fig. 19.15. Along such a path there is a gradual transition from the liquid to the gas region. This occurs without any abrupt change in properties.

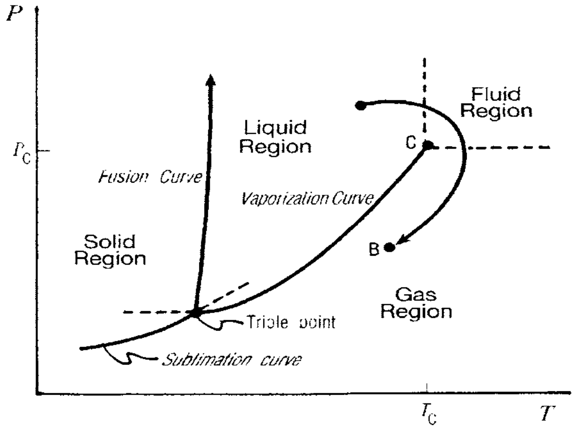

Fig. 19.15 P, T–diagram of a pure substance

19.16 Phase Transitions in Simple Systems – The Phase Rule

The phase rule, due to Gibbs, connects the number of phases that are possible in any thermodynamic system with the number of components of the system and with the number of thermodynamic variables that characterize it.

We consider c components distributed over ϕ phases of a simple system[17]. The conditions of phase equilibrium (cf. § 19.12) become

$$\mu^{\alpha}(T, P) = \mu^{\beta}(T, P) = \ldots = \mu^{\phi}(T, P). \qquad (19.16)_1$$

Since thus all ϕ potentials are determined if one is known, this provides $\phi - 1$ equations. Hence, the total number of equations that must be satisfied for c components is $c(\phi - 1)$. The most convenient set of parameters with which to characterize the system consists of the

---

[17] The rule may, of course, be extended to non-simple systems (cf. § 19.18).

intensive parameters, i.e., the temperature, the pressure, and the mole fractions. Because the latter compositional variables are related by $\Sigma_j \overline{n}_j = 1$, we need to know $c - 1$ mole fractions, i.e., $\phi(c-1)$ fractions for ϕ phases. Adding the temperature and pressure, this makes $\phi(c-1)+2$ the number of intensive parameters capable of independent variation. If there are more equations than independent variables, no solution exists, i.e., no equilibrium is possible under those circumstances. When the number of independent variables exactly matches the number of equations, there is a unique solution for one temperature, pressure, and composition of the phases. If there are more independent variables than phases, equilibrium is possible for certain manifolds of states. The number by which the independent variables exceed the number of phases is the number of degrees of freedom, f. This is the number of independently variable intensive parameters of the system [cf. § 8.7]. We have

$$\mathrm{f} = 2 + \phi(c-1) - c(\phi - 1) \tag{19.16$_2$}$$

or

$$\mathrm{f} + \phi = c + 2\,. \tag{19.16$_3$}$$

Equation (19.16)$_3$ embodies Gibbs's phase rule for the simple system. For a pure substance, $c = 1$. The maximum number of phases in a simple system is therefore three, and that number is possible only if the number of degrees of freedom is zero. Hence the point at which all phases coexist is a *triple* point.

19.17 Phase Transitions in Multicomponent Systems – The Binary Solution

Excepting the preceding section we have, so far, considered single-component systems only. As the simplest example of a multicomponent system we shall now consider a binary system, and we select the case of a binary solution as one of the most frequently encountered such systems. Extension to systems with more than two components is straightforward in principle.

In the system under consideration we are primarily interested in compositional changes at constant (normally atmospheric) pressure and at different constant temperatures. It is therefore convenient to diagram these changes as constant pressure isotherms of one of the two chemical potentials as function of the mole fraction of the corresponding component in the solution. Such isotherms are shown in Fig. 19.17.

The plot shows many similarities to that displayed in Fig. 19.2. Above a critical point, here called the *consolute point*, the two components are miscible in all proportions. At lower temperatures the solution separates into two phases. There is again a spinodal as well as a binodal curve, and analog considerations of stability apply, except that the highest order criterion now is the criterion of diffusional stability that we have introduced in § 18.11

$$\left.\frac{\partial \mu_1}{\partial \overline{n}_1}\right|_{T,P} \geq 0\,. \tag{19.17$_1$}$$

As was pointed out there, at any given temperature an increase in the mole fraction of a component increases its chemical potential.

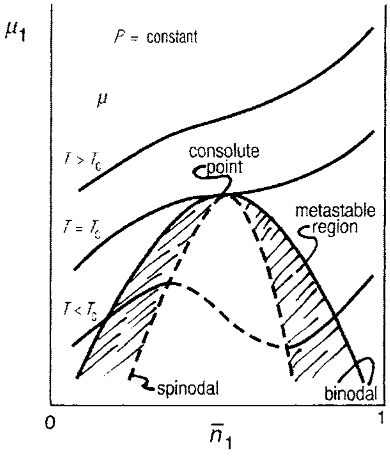

Fig. 19.17 Chemical potential vs. composition for a binary system

On the spinodal

$$\left.\frac{\partial \mu_1}{\partial \bar{n}_1}\right|_{T,P} = \left.\frac{\partial^2 \mu_1}{\partial \bar{n}_1^2}\right|_{T,P} = 0, \qquad \left.\frac{\partial^3 \mu_1}{\partial \bar{n}_1^3}\right|_{T,P} > 0 \qquad (19.17)_2$$

and the consolute point is a point of stable equilibrium.

19.18 Phase Transitions in Non-Simple Systems

The phase rule is valid in the form given by Eq.$(19.16)_3$ only for a multicomponent *simple* system. The constant 2 appears because the only intensive parameters considered apart from the mole fractions are the temperature and pressure. If, e.g., magnetic field intensity is also to be taken into account, the constant would be 3.

19.19 Higher-Order Phase Transitions

The phase transitions we discussed in the preceding sections involved discontinuous changes in the volume, V, and the entropy, S, respectively. Clapeyron's equation, Eq.$(19.12)_4$, relates the change of pressure with temperature to these discontinuous changes in the entropy and the volume. The latter quantities are the first-order derivatives of the free enthalpy, G. Phase transitions that show discontinuities in these first-order derivatives are called *first-order transitions*.

A *second-order transition* occurs when the second-order derivatives of G, i.e., the members of the primary set (cf. § 10.2) of second-order partial derivatives, α_P, κ_T, and C_P, are discontinuous while the first-order ones remain continuous.

Higher-order transitions may be defined similarly. The classification is due to Ehrenfest who also introduced the equation

$$\frac{dP}{dT} = \frac{\Delta \alpha_P}{\Delta \kappa_T} = \frac{\Delta C_P}{TV\Delta \alpha} \tag{19.19}$$

as the analog of the Clapeyron equation for a second-order phase transition. While some second-order phase transitions appear to exist (superconductors in zero magnetic field are reputed to show such transitions), there does not seem to be any evidence for the existence of transitions of order higher than the second.

Some transitions have many of the features of second-order transitions in the Ehrenfest sense but are, in fact, kinetic phenomena and not true thermodynamic second-order transitions. A point in case is the so-called *glass transition* in high polymers.

20. CHEMICAL REACTIONS

Previous chapters were concerned with *non-reactive* systems. We now turn to an examination of the equilibrium thermodynamics of systems in which chemical reactions occur, i.e., *reactive* systems. Chemical reactions produce changes in composition and, therefore, entail *mass action*. They also either evolve or absorb heat. There is therefore production of entropy in at least some part of the system and chemical reactions are thus inherently irreversible processes. Much of the theory of chemical reactions can, however, be discussed within the framework of classical equilibrium thermodynamics and this discussion forms the subject of Chapters 20 and 21, the last chapters of Part I of this text. In these chapters some concepts will be introduced which will recur in the theory of chemical reactions as irreversible processes which forms the subject of Chapter 22, the first chapter of Part II. The equilibrium thermodynamics of chemical reactions may thus be considered to form a transition to irreversible thermodynamics.

20.0 Chapter Contents

20.1 The Reactive Simple System

The reactive simple system is a closed simple system in which chemical reactions take place. We may consider a chemical reaction to occur as the result of removing some constraint that had hitherto prevented the components, as the case may be, either from dissociating, or from reacting with each other. The removal of the barrier might be visualized as being brought about by the introduction of a catalyst.

We consider the reactive simple system to be initially in equilibrium with respect to temperature and pressure. It is not, however, in *chemical equilibrium*, i.e., in equilibrium with respect to the distribution of matter among the reactants and products of the chemical reaction, and is thus only in *partial equilibrium*. Reactions are thus spontaneous, hence irreversible, processes, resulting in an increase in the entropy of the system. The latter generally evolves or absorbs heat in the course of the reaction and this is the source of the irreversibility. A simple example is a mixture of ideal gases that react chemically. The concentration (amount per unit volume) of each species is uniform throughout the reaction volume but at any instant during the reaction the concentrations are not those that exist at chemical equilibrium.

20.2 The Stoichiometric Equation

Since the reactive simple system is closed, the change in the mole numbers of the components occurs only by dint of the reaction and is expressed by the *stoichiometric* (or *chemical*) *equation*

$$\sum_{j=1}^{j=r} |\nu_j|\,\Omega_j \rightleftharpoons \sum_{j=r+1}^{j=n} |\nu_j|\,\Omega_j \tag*{(20.2)$_1$}$$

in which the Ω_j are the *chemical symbols* of the various compounds, and the ν_j are the *stoichiometric coefficients*. The latter are the smallest possible integers which will balance the equation.

By convention, the quantities on the left represent the *reactants* and those on the right the *products*. By affixing negative signs to the stoichiometric coefficients of the reactants and then transferring them to the right hand side of Eq.(20.2)$_1$, the stoichiometric equation becomes

$$\sum_{j=1}^{j=n} \nu_j\,\Omega_j = 0\,. \tag*{(20.2)$_2$}$$

The stoichiometric equation represents the relative amounts of the components of the reactive simple system at equilibrium [cf. Eq.(21.1)$_2$].

20.3 The Stoichiometric Equation: An Example

To illustrate, let us consider the reaction having the stoichiometric equation

$$3H_2 + SO_2 \rightleftharpoons H_2S + 2H_2O\,. \tag*{(20.3)$_1$}$$

Here, $\Omega_1 = H_2$, $\Omega_2 = SO_2$, $\Omega_3 = H_2S$, and $\Omega_4 = H_2O$. Letting $\nu_1 = -3$, $\nu_2 = -1$, $\nu_3 = 1$, and $\nu_4 = 2$, the reaction may be written

$$-3\Omega_1 - \Omega_2 + \Omega_3 + 2\Omega_4 = 0 \tag*{(20.3)$_2$}$$

in accordance with Eq.(20.2)$_2$.

20.4 The Extent of Reaction

We now introduce the important concept of the *extent of reaction*. Because of the stoichiometry of the reaction, changes in the mole numbers of any two components are related to each other through their respective stoichiometric coefficients. Thus,

$$\frac{dN_j}{dN_k} = \frac{\nu_j}{\nu_k} \tag*{(20.4)$_1$}$$

or

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \ldots = \frac{dN_n}{\nu_n}\,. \tag{20.4)_2}$$

Since these ratios are all equal to each other[18], they may all be equated to a quantity $d\xi$. We may write

$$\frac{dN_j}{\nu_j} = d\xi\,. \tag{20.4)_3}$$

Here ξ expresses the amount or extent to which the reaction as a whole has proceeded, and was called the *degree of the advancement of the reaction*[19] by de Donder (1936). Equivalent terms are the *extent* (or *amount*) *of reaction*, or the *reaction coordinate*. For Eq.(20.3)$_2$ we find

$$\frac{dN_{H_2}}{-3} = \frac{dN_{SO_2}}{-1} = \frac{dN_{H_2S}}{1} = \frac{dN_{H_2O}}{2} = d\xi\,. \tag{20.4)_4}$$

At any instant, ξ is an extensive variable of state. The concept of the reaction coordinate can be extended to phase transitions as well as to order-disorder phenomena such as, e.g., the rearrangement of copper and zinc atoms in brass [Denbigh, 1966]. It is, therefore, also called the *order parameter*.

20.5 The Affinity: Change in Mass Action in a Reactive System

With the help of Eq.(20.4)$_3$ we see that the change in mass action in a reactive simple system becomes

$$\delta M = \sum\nolimits_j \mu_j\, dN_j = \left(\sum\nolimits_j \mu_j\, \nu_j\right) d\xi\,. \tag{20.5)_1}$$

We now introduce the *affinity* of the chemical reaction,

$$A = -\sum\nolimits_j \mu_j\, \nu_j \tag{20.5)_2}$$

(de Donder, 1928). The affinity is the driving force of the chemical reaction. It is positive if the reaction proceeds spontaneously from the left to the right of the stoichiometric equation and negative conversely. Being a weighted sum of chemical potentials, the affinity is an

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[18] Obviously, these relations are valid only in a closed system.

[19] This should not be confused with the *degree of reaction*. See Callen (1963), p. 202, (1985), p.169.

intensive parameter. It is, however, not an independent physical variable like the temperature or pressure because it depends on the state of the system at any particular instance.

With the help of the affinity, A, and the extent of reaction, ξ, we may now write

$$\delta M = -Ad\xi \tag{20.5$_3$}$$

for the change in the mass action term in a chemical reaction. The introduction of A and ξ will allow us to identify the infinitesimal change in the internally generated heat, $\delta Q'$, in a chemical reaction with the mass action term [cf. Eq.(22.1)$_4$].

20.6 The Basic Thermodynamic Equations for Chemical Reactions

In the reactive simple system the negative products of the affinity with the extent of reaction replace the products of the chemical potential and the mole numbers. Thus, in the energy representation the Euler form of the fundamental equation of the reactive simple system becomes

$$U = TS - PV - A\xi\,. \tag{20.6$_1$}$$

Its differential form and those of the usual Legendre transforms follow as

$$dU = TdS - PdV - Ad\xi\,, \tag{20.6$_2$}$$
$$d\mathrm{H} = TdS + VdP - Ad\xi\,, \tag{20.6$_3$}$$
$$d\mathrm{F} = -SdT - PdV - Ad\xi\,, \tag{20.6$_4$}$$
$$d\mathrm{G} = -SdT + VdP - Ad\xi\,. \tag{20.6$_5$}$$

The Gibbs-Duhem equation for the reactive simple system is given by

$$SdT - VdP - \xi dA = 0\,. \tag{20.6$_6$}$$

In the entropy representation the Euler equation of the reactive simple system becomes

$$S = \frac{1}{T}U + \frac{P}{T}V + \frac{A}{T}\xi\,, \tag{20.6$_7$}$$

and its differential form is

$$dS = \frac{1}{T}dU + \frac{P}{T}dV + \frac{A}{T}d\xi\,. \tag{20.6$_8$}$$

The various Massieu functions, their differential forms, and the Gibbs-Duhem equation in the entropy representation are easily obtained but will not be needed here.

20.7 The Heat of Reaction at Constant Pressure

During a chemical reaction heat is either evolved or absorbed. In the first case the reaction is *exothermic*, in the second case it is *endothermic*. At constant pressure this *heat of reaction* represents the change in the enthalpy, ΔH, of the reacting system. This change is positive in exothermic, and negative in endothermic reactions. It can be obtained from C_P, the heat capacity at constant pressure of the reaction mixture, by *Kirchhoff's equation*

$$\Delta H = \int_{T_1}^{T_2} C_P(T)\, dT \,. \tag{20.7$_1$}$$

To understand the meaning of ΔH more clearly, consider that it is the change of the enthalpy with the extent of reaction at constant temperature and pressure. Thus,

$$\left.\frac{\partial H}{\partial \xi}\right|_{T,P} = \sum\nolimits_j \left.\frac{\partial H}{\partial N_j}\right|_{T,P} \frac{dN_j}{d\xi} = \sum\nolimits_j \nu_j \overline{H}_j = \Delta H \,, \tag{20.7$_2$}$$

where $\overline{H}_j$ is the partial molar enthalpy of component j at the temperature T.

In terms of the affinity, A, Eq.(20.6)$_3$ yields

$$\Delta H = \left.\frac{\partial H}{\partial \xi}\right|_{T,P} = T\left.\frac{\partial A}{\partial T}\right|_{P,\xi} - A \tag{20.7$_3$}$$

where we have used the Maxwell relation

$$\left.\frac{\partial S}{\partial \xi}\right|_{T,P} = \left.\frac{\partial A}{\partial T}\right|_{P,\xi} . \tag{20.7$_4$}$$

Near equilibrium the affinity will become vanishingly small (cf. § 21.1)). However, its temperature derivative does not vanish. Close to equilibrium, therefore,

$$\Delta H = \left.\frac{\partial H}{\partial \xi}\right|_{T,P} = T\left.\frac{\partial A}{\partial T}\right|_{P,\xi} . \tag{20.7$_5$}$$

This identity is justified because the affinity is positive if the reaction proceeds from the left to the right of the stoichiometric equation at constant pressure (ΔH is exothermic), and is negative in the opposite direction (ΔH is endothermic).

20.8 The Heat of Reaction at Constant Volume

An entirely analogous derivation starting from Eq.$(20.6)_2$ instead of $(20.6)_3$ produces

$$\left.\frac{\partial U}{\partial \xi}\right|_{V,P}=T\left.\frac{\partial A}{\partial T}\right|_{V,\xi}=\Delta U \tag{20.8}$$

where $\Delta U=\Sigma_j \nu_j \overline{U}_j$ is the change in internal energy when the reaction proceeds at constant volume, and $\overline{U}_j$ is the partial molar internal energy of component j at constant temperature.

21. REACTION EQUILIBRIUM

The concepts of the extent of reaction and of de Donder's affinity greatly simplify the thermodynamics of chemical reactions. We make use of both of these concepts as we inquire into the nature of *reaction* (or *chemical*) *equilibrium*. We then inquire into the determination of the composition at equilibrium. This requires the notion of equilibrium constants. We further introduce the equation of van't Hoff which relates the equilibrium constants to the heat of reaction, and we examine the stability of chemical reactions and the effects of temperature and pressure on reaction equilibrium. Finally, we consider simultaneous reactions and their additivity.

21.0 Chapter Contents

21.1 The Equation of Chemical Equilibrium

At constant temperature and pressure Eq.$(20.6)_5$ reduces to

$$dG = -A d\xi \,. \qquad (21.1)_1$$

At equilibrium dG must vanish for an arbitrary value of $d\xi$, and the condition for reaction equilibrium is therefore expressed by $A = 0$. The condition demands that the affinity, the driving force of the reaction, vanish at equilibrium. Equation $(20.5)_2$ then becomes

$$\sum_j \mu_j \nu_j = 0 \,. \qquad (21.1)_2$$

Tbhis equationis called the *equation of chemical equilibrium*. It is analogous to the condition of diffusional (matter flow) equilibrium, $\mu_1 = \mu_2$ [cf. Eq.$(4.6)_{3.3}$]. Comparison with Eq.$(20.2)_2$ shows that the equation of chemical equilibrium may be obtained from the stoichiometric equation simply by substituting the jth chemical potential, μ_j, for the jth chemical symbol, Ω_j.

21.2 The Equilibrium Constant $\mathrm{K_p}(T)$

The question now arises: what is the equilibrium composition in a reactive system? To answer this question we introduce the concept of the *equilibrium constant* and to do this, we need to know the integrated form of the Gibbs-Duhem equation for a reactive simple system, i.e.,

$$\mu_j = \mu_j(T, P, A)\,. \qquad (21.2)_1$$

In reactions between ideal gases the situation is particularly transparent. In that case the chemical potential of the jth component [cf. Eq.(15.12)$_3$] is

$$\mu_j = \mu_{\mathrm{o}j}(T) + \mathrm{R}T\, ln\, P_j \qquad (21.2)_2$$

considering the standard pressure, P_{o}, to be unity. Multiplying by ν_j and summing yields

$$\sum\nolimits_j \nu_j \mu_j = \sum\nolimits_j \nu_j\, \mu_{\mathrm{o}j}(T) + \mathrm{R}T\, ln \prod\nolimits_j P_j^{\nu_j} \qquad (21.2)_3$$

or, using Eq.(20.5)$_2$,

$$A = A_{\mathrm{o}}(T) - \mathrm{R}T\, ln \prod\nolimits_j P_j^{\nu_j} \qquad (21.2)_4$$

where

$$A_{\mathrm{o}}(T) = -\sum\nolimits_j \nu_j\, \mu_{\mathrm{o}j}(T) \qquad (21.2)_5$$

is the *standard affinity* at unit standard pressure, P_{o}.

At equilibrium the affinity vanishes and we have

$$A_{\mathrm{o}}(T) = \mathrm{R}T\, ln \prod\nolimits_j P_j^{\nu_j}\,. \qquad (21.2)_6$$

Let us introduce

$$\mathrm{K_p}(T) = \prod\nolimits_j P_j^{\nu_j} \qquad (21.2)_7$$

as the *equilibrium constant* of the reaction. Substituting it into Eq.(21.2)$_4$ leads to

$$A_{\mathrm{o}}(T) = \mathrm{R}T\, ln\, \mathrm{K_p}(T) \qquad (21.2)_8$$

and introducing this into Eq.$(21.2)_4$ gives

$$\mathrm{K_p}(T) = \prod\nolimits_j P_j^{\nu_j} \exp\left(\frac{A}{\mathrm{R}T}\right) . \qquad (21.2)_9$$

which relates the equilibrium constant to the affinity.

The subscript p on $\mathrm{K_p}(T)$ indicates that it is expressed in terms of the partial pressures of a gas. In this form the equilibrium constant depends on the temperature only. Since $\mu_j^{\mathrm{sol}} = \mu_j^{\mathrm{vap}}$ by the condition of phase equilibrium, Eq.$(21.2)_8$ is also valid for solutions, at least as long as the vapor can be considered to be ideal. The P_j's then stand for the partial vapor pressures above the solution.

21.3 The Equilibrium Constants $\mathrm{K}_{\bar{n}}(T, P)$ and $\mathrm{K_c}(T)$

The equilibrium constant can be formulated in terms of parameters other than the partial pressures. If the gases or vapors can be considered ideal, the relation $P_j = P\bar{n}_j$ (cf. § $15.8)_2$ yields

$$\mathrm{K}_{\bar{n}}(T, P) = \prod\nolimits_j \bar{n}_j^{\nu_j} = P^{-\bar{\nu}}\, \mathrm{K_p}(T) \qquad (21.3)_1$$

where $\bar{\nu} = \Sigma_j \nu_j$. $\mathrm{K}_{\bar{n}}(T, P)$ is the equilibrium constant of the reaction in terms of the mole fractions. It is independent of pressure only when $\bar{\nu} = 0$ as it is, for instance, in the reaction $H_2 + Cl_2 = 2HCl$. Using the relation $P_j = \mathrm{c}_j \mathrm{R}T$ where $\mathrm{c}_j = N_j/V$ is the molar concentration[20], we derive

$$\mathrm{K_c}(T) = \prod\nolimits_j \mathrm{c}_j^{\nu_j} = (\mathrm{R}T)^{-\bar{\nu}}\, \mathrm{K_p}(T) , \qquad (21.3)_2$$

for the equilibrium constant in terms of the molar concentrations.

Elimination of $\mathrm{K_p}(T)$ between the last two equations yields

$$\mathrm{K}_{\bar{n}}(T, P) = (\mathrm{R}T/P)^{\bar{\nu}}\, \mathrm{K_c}(T) \qquad (21.3)_3$$

as the relation linking the equilibrium constants $\mathrm{K}_{\bar{n}}(T, P)$ and $\mathrm{K_c}(T)$.

21.4 The Equilibrium Composition

To obtain now the composition at equilibrium, we integrate Eq.$(20.4)_3$ to yield

$$N_j = N_{oj} + \nu_j\, \Delta\xi , \qquad (21.4)$$

---

[20] The molar concentration is often assigned the symbol $[\Omega_j]$.

where N_{oj} is the initial number of moles of the jth species, and $N_j = N\bar{n}_j$ is the final number of the same species after the reaction has reached equilibrium. Thus, prediction of the equilibrium composition requires knowledge of only a single number, $\Delta\xi$. We proceed to relate this to the equilibrium constant, $K_p(T)$.

21.5 The Equilibrium Composition: An Example

The procedure to be followed in finding the N_j's is best considered on hand of an example. We use the reaction whose stoichiometric equation is given by Eq.(20.3)$_1$. For this reaction the equation of chemical equilibrium, Eq.(21.1)$_2$, becomes

$$-3\mu_{H_2} - \mu_{SO_2} + \mu_{H_2S} + 2\mu_{H_2O} = 0\,. \qquad (21.5)_1$$

Suppose the initial composition consist of the following mole numbers:

$$\begin{array}{ll} N_{H_2} & = 2 \\ N_{SO_2} & = 1 \\ N_{H_2S} & = 0.5 \\ N_{H_2O} & = 0.75 \end{array}$$

and the temperature and pressure are such that the gases may be considered ideal. Then, since by Eq.(21.4) we have $N_j = N_{oj} + \nu_j\Delta\xi$, the composition at equilibrium becomes

$$\begin{array}{llcr} N_{H_2} & = 2 & - & 3\Delta\xi \\ N_{SO_2} & = 1 & - & \Delta\xi \\ N_{H_2S} & = 0.5 & + & \Delta\xi \\ N_{H_2O} & = 0.75 & + & 2\Delta\xi \end{array}$$

and the total number of moles, $\Sigma_j N_j = N$, is $4.25 - \Delta\xi$.

Now, by Eq.(21.3)$_1$ the equilibrium constant, $K_p(T)$, may be recast as

$$K_p(T) = P^{\bar{\nu}} \prod\nolimits_j \bar{n}_j^{\nu_j} = (P/N)^{\bar{\nu}} \prod\nolimits_j N_j^{\nu_j} \qquad (21.5)_2$$

and, since $\bar{\nu} = \Sigma_j \nu_j = -1$ (cf. § 20.3), we find

$$K_p(T) = P^{-1}\frac{(0.5+\Delta\xi)(0.75+\Delta\xi)^2}{(2-3\Delta\xi)^3(1-\Delta\xi)}(4.25-\Delta\xi)\,. \qquad (21.5)_3$$

This can be solved for $\Delta\xi$. Substitution of the result into the equations for the mole numbers then yields the composition at equilibrium.

21.6 van't Hoff's Equation

It is of interest to relate the temperature coefficient of the equilibrium constant to the heat of reaction, ΔH. By Eqs.(20.7)$_3$ and (20.7)$_9$ we have

$$\Delta H = T\frac{\partial A}{\partial T}\bigg|_{P,\xi} - A \tag{21.6)$_1$}$$

and

$$A = \mathrm{R}T\, ln \frac{\mathrm{K_p}(T)}{\prod_j P_j^{\nu_j}}\,. \qquad (21.6)_2$$

Combining the two leads to

$$\Delta H = T\frac{\partial A}{\partial T}\bigg|_{P,\xi} - \mathrm{R}T\, ln \frac{\mathrm{K_p}(T)}{\prod_j P_j^{\nu_j}} \qquad (21.6)_3$$

and integration with respect to T at constant P and ξ gives

$$\Delta H = -A + \mathrm{R}T\, ln \frac{\mathrm{K_p}(T)}{\prod_j P_j^{\nu_j}} + \mathrm{R}T^2 \frac{\mathrm{d}\, ln\, \mathrm{K_p}(T)}{dT}\,. \qquad (21.6)_3$$

At equilibrium the first two terms on the right vanish by Eq.(21.6)$_2$ and we obtain *van't Hoff's equation*

$$\frac{\mathrm{d}\, ln\, \mathrm{K_p}(T)}{dT} = \frac{\Delta H}{\mathrm{R}T^2} \qquad (21.6)_4$$

which is the desired relation between the temperature coefficient of the equilibrium constant and the heat of reaction. It implies that $\mathrm{K_p}(T)$ increases with temperature in endothermic, and decreases with it in exothermic reactions. We note the formal resemblance of van't Hoff's equation and the Clausius-Clapeyron equation as given by Eq.(19.13)$_5$.

By Eq.(21.3)$_2$

$$\mathrm{K_p}(T) = (\mathrm{R}T)^{\bar{\nu}}\, \mathrm{K_c}(T)\,. \qquad (21.6)_5$$

But we also have $\Delta H = \Sigma_j \nu_j \overline{H}_j$ and, since we are considering ideal gases, $\overline{H}_j = \overline{U}_j + \mathrm{R}T$. Hence,

$$\frac{\mathrm{d}\, ln\, \mathrm{K_c}(T)}{dT} = \frac{\Delta \mathrm{U}}{\mathrm{R}T^2} \qquad (21.6)_6$$

is another form of van't Hoff's equation. Determination of $K_c(T)$ as a function of temperature therefore allows calculation of ΔU and, hence, ΔH, from concentration measurements instead of the more difficult calorimetric measurements required for the determination of $K_p(T)$.

21.7 The Stability of Chemical Reactions

The stability criterion for chemical reactions is

$$y_{33}^{(2)} > 0 \tag{21.7)$_1$}$$

where $y^{(0)} = U(S, V, \xi)$ is the base function. Therefore, the criterion takes the form

$$G_{\xi\xi} = -\left.\frac{\partial A}{\partial \xi}\right|_{T,P} > 0 \qquad (21.7)_2$$

or

$$\left.\frac{\partial A}{\partial \xi}\right|_{T,P} < 0\,. \qquad (21.7)_3$$

Thus the affinity decreases as the extent of reaction increases. In the limit of stability $A = 0$ and we obtain the criterion of reaction equilibrium in the form $G_{\xi\xi} = 0$.

It is possible to have

$$\left.\frac{\partial A}{\partial \xi}\right|_{T,P} > 0\,. \qquad (21.7)_4$$

The affinity then increases as ξ increases. This is the case of an unstable, i.e., 'run-away' reaction.

21.8 Effect of Temperature on Reaction Equilibrium

Let us now consider the stability of chemical reactions in the light of Le Châtelier's principle. We first consider variations in ξ with temperature at constant pressure, i.e., $(\partial\xi/\partial T)_{P,A}$. Using the chain rule for partial differentiation, we obtain

$$\left.\frac{\partial \xi}{\partial T}\right|_{P,A} = -\left.\frac{\partial \xi}{\partial A}\right|_{T,P}\left.\frac{\partial A}{\partial T}\right|_{P,\xi}\,. \qquad (21.8)_1$$

Using Eq.$(20.7)_5$ for the second derivative on the right gives by

$$\left.\frac{\partial \xi}{\partial T}\right|_{P,A} = -\frac{1}{T}\left.\frac{\partial H}{\partial \xi}\right|_{T,P}\left.\frac{\partial \xi}{\partial A}\right|_{T,P} . \qquad (21.8)_2$$

But $1/T$ is > 0 by definition and

$$-\left.\frac{\partial \xi}{\partial A}\right|_{T,P} > 0 \qquad (21.8)_3$$

by the stability criterion, Eq.$(21.7)_3$. Paying attention only to the sign of the expressions, we have

$$\operatorname{sgn}\left.\frac{\partial \xi}{\partial T}\right|_{P,A} = \operatorname{sgn}\left.\frac{\partial H}{\partial \xi}\right|_{T,P} \qquad (21.8)_4$$

The relation above shows that an increase in temperature increases the extent of reaction for an endothermic reaction and decreases it for an exothermic one. An increase in the temperature at constant pressure therefore shifts the chemical equilibrium in the direction in which the system absorbs heat, in accordance with Le Châtelier's principle (cf. § 18.7)..

21.9 The Effect of Pressure on Reaction Equilibrium

Next, we consider variations in ξ with pressure at constant temperature, i.e., $(\partial\xi/\partial P)_{P,A}$. This is given by

$$\left.\frac{\partial \xi}{\partial P}\right|_{T,A} = -\left.\frac{\partial A}{\partial P}\right|_{T,\xi}\left.\frac{\partial \xi}{\partial A}\right|_{T,P} , \qquad (21.9)_1$$

and, using the Maxwell relation given by Eq.$(A2.2)_9$ for the first term on the right, we obtain

$$\left.\frac{\partial \xi}{\partial P}\right|_{T,A} = \left.\frac{\partial V}{\partial \xi}\right|_{T,P}\left.\frac{\partial \xi}{\partial A}\right|_{T,P} . \qquad (21.9)_2$$

By virtue of Eq.$(21.8)_3$ we thus find

$$\operatorname{sgn}\left.\frac{\partial \xi}{\partial P}\right|_{T,A} = -\operatorname{sgn}\left.\frac{\partial V}{\partial \xi}\right|_{T,P} . \qquad (21.9)_3$$

Hence, again in accordance with Le Châtelier's principle, increasing the pressure at constant temperature shifts the chemical equilibrium in the direction in which the total volume decreases.

21.10 Simultaneous Reactions

It is easy to extend the formalism for a single reaction to that for several simultaneous reactions. Let there be p reactions among the r constituents of the reactive simple system. There is an equation of chemical equilibrium for each reaction, i.e., we have

$$\sum\nolimits_j \mu_j \nu_j^{(k)} = 0 \qquad (21.10)_1$$

where the superscript (k) marks the kth reaction. We further have

$$\Delta N_j^{(k)} = \nu_j^{(k)}\, \Delta\xi^{(k)}. \qquad (21.10)_2$$

Thus, there are k equations for the k unknowns $\Delta\xi^{(k)}$ which, in turn, by

$$N_j = N_{oj} + \sum\nolimits_j \nu_j^{(k)}\, \Delta\xi^{(k)}\,. \qquad (21.10)_3$$

determine all the mole numbers at equilibrium.

21.11 Additivity of Reactions

Let there be given two reactions,

$$\sum\nolimits_j \nu_j^{(1)}\, \Omega_j = 0 \quad \text{and} \quad \sum\nolimits_j \nu_j^{(2)}\, \Omega_j = 0\,. \qquad (21.11)_1$$

Now consider a third reaction,

$$\sum\nolimits_j \nu_j^{(3)}\, \Omega_j = \sum\nolimits_j \left[a\, \nu_j^{(1)} \;+\; b\, \nu_j^{(2)}\right] \Omega_j\,, \qquad (21.11)_2$$

that is a combination of the first two, a and b being arbitrary positive integers.

Combining Eqs.$(21.2)_3$ and $(21.2)_7$ gives

$$\sum\nolimits_j \nu_j^{(k)} \mu_j = \sum\nolimits_j \nu_j^{(k)} \mu_{oj}(T) + \mathrm{R}T\, ln\, \mathrm{K_p}(T)\,, \qquad (21.11)_3$$

and, since $\Sigma_j \mu_j \nu_j = 0,$ we find

$$ln\, \mathrm{K}_1(T) = -(1/\mathrm{R}T)\sum_j \nu_j^{(1)}\, \mu_{oj}(T) \qquad (21.11)_4$$

$$ln\, \mathrm{K}_2(T) = -(1/\mathrm{R}T)\sum_j \nu_j^{(2)}\, \mu_{oj}(T)\,. \qquad (21.11)_5$$

and

$$ln\, \mathrm{K}_3(T) = -(1/\mathrm{R}T)\sum_j \left[a\, \nu_j^{(1)} + b\, \nu_j^{(2)}\right]\mu_{oj}(T) \qquad (21.11)_6$$

i.e.,

$$ln\, \mathrm{K}_3(T) = a\; ln\, \mathrm{K}_1(T) + b\; ln\, \mathrm{K}_2(T)\,. \qquad (21.11)_7$$

It follows that the constants for additional reactions that are combinations of the known ones, can be obtained directly if the equilibrium constants are known for some reactions.

22. CHEMICAL REACTIONS AS IRREVERSIBLE PROCESSES

Chapters 20 and 21 dealt with the equilibrium thermodynamics of chemical reactions. A chemical reaction is an irreversible process and is therefore invariably accompanied by the production of entropy. It is the task of Chapter 22 to examine chemical reactions as irreversible processes. This undertaking necessarily leads to the introduction of a number of concepts that are required in the treatment of the thermodynamics of the *steady state,* such as, in particular, the *entropy production, energy dissipation,* and *energy retention functions.* A consideration of chemical reactions as irreversible processes thus constitutes a natural transition from equilibrium to steady-state thermodynamics.

22.0 Chapter Contents

22.1 De Donder's Inequality

Consider a chemical reaction taking place in a vessel that is closed but not isolated. It can thus exchange heat but not matter with its surroundings. By Eq.(5.6)$_1$ the infinitesimal change in entropy becomes

$$dS = \delta Q/T + \delta Q'/T = d_e S + d_i S\,, \tag{22.1$_1$}$$

and substituting this equation into Eq.(20.6)$_8$ leads to

$$d_e S + d_i S = \frac{dU + PdV}{T} + \frac{Ad\xi}{T}\,. \tag{22.1$_2$}$$

In the absence of any entropy produced within the reaction vessel, we would simply have

$$Td_e S = \delta Q = dU + PdV\,. \tag{22.1$_3$}$$

If, however, entropy is generated within the vessel [cf. Eq.$(5.6)_2$] we additionally have the heat term

$$Td_iS = \delta Q' = Ad\xi \geq 0 . \qquad (22.1)_4$$

The last relation is *de Donder's inequality*. It identifies the internally generated heat, $\delta Q'$, in a chemical reaction with the mass action term, $Ad\xi$, and states that this is positive semi-definite. It is zero when the internal changes are reversible, and positive when they are irreversible.

22.2 The General Criterion of Irreversibility

Since d_iS represents *production of entropy*, de Donder's inequality in the form

$$d_iS > 0 \qquad (22.2)$$

is a criterion of irreversibility. It is also the only *general* criterion of irreversibility.

22.3 Particular Criteria of Irreversibility

Criteria applicable under particular conditions are readily obtained from the Gibbs equation for the internal energy, U, and its first-order Legendre transforms. The changes in the thermodynamic potentials are given by Eqs. $(20.6)_2$ to $(20.6)_5$. We have, therefore,

$$\left.\frac{\partial U}{\partial \xi}\right|_{S,V} = \left.\frac{\partial H}{\partial \xi}\right|_{S,P} = \left.\frac{\partial F}{\partial \xi}\right|_{T,V} = \left.\frac{\partial G}{\partial \xi}\right|_{T,P} = -A \qquad (22.3)_1$$

and

$$dU = dH = dF = dG < 0 \qquad (22.3)_2$$

as the *criteria of irreversibility* in terms of the thermodynamic potentials U, H, F, and G, i.e., at constant S and V, constant S and P, constant T and V, and constant T and P, respectively. By these criteria all four potentials necessarily decrease as a chemical reaction takes place.

22.4 The Rate of Reaction

During the course of a reaction the extent of reaction, introduced in § 20.4, evolves with time until equilibrium is reached. The time derivative of the evolving extent of reaction is called the *rate of reaction*, *v*. The rate of reaction depends not only on the time but also on the temperature, T, and on the pressure, P. These latter may be arbitrary functions of time, i.e., we may have $T = T(t)$, and $P = P(t)$. However, if these functions are specified, the rate of reaction is completely determined and we may write simply

$$v = \frac{d\xi}{dt}\,. \tag{22.4$_1$}$$

Now, by de Donder's inequality, $Ad\xi \geq 0$, we have

$$A\frac{d\xi}{dt} = Av \geq 0 \tag{22.4$_2$}$$

whence,

if	then
$A > 0$	$v \geq 0$
$A = 0$	$v = 0$
$A < 0$	$v \leq 0$

Thus, the affinity has the same sign as the rate of reaction. If the affinity is zero, the rate of reaction is also zero, i.e., the system is at equilibrium. The latter follows because, if $v \neq 0$ when $A = 0$, the reaction would proceed with a finite rate at equilibrium, which is contradictory. Note, however, that we may have $v = 0,\ A \neq 0$. The system is then in *false equilibrium* (e.g., a mixture of gaseous hydrogen, H_2, and oxygen, O_2).

22.5 The Rate of Entropy Production

We now introduce three important new concepts related to the rate of reaction. The *rate of entropy production*, Θ, i.e., the entropy produced per unit time, is

$$\Theta = \frac{d_iS}{dt} = \frac{\delta Q'}{Tdt} = \frac{A}{T}\frac{d\xi}{dt} = \frac{A}{T}v > 0\,. \tag{22.5}$$

It is positive definite because of the thermodynamic irreversibility of any chemical reaction.

22.6 The Entropy Production Function

The entropy produced per unit time and unit volume, i.e., the rate of entropy production per unit volume, is called the *entropy production function*, or the *entropy source density*, or the *entropy source strength*. It becomes

$$\Phi = \frac{\Theta}{V} = \frac{A}{VT}v > 0 \tag{22.6}$$

and is again positive definite in any single chemical reaction.

22.7 The Energy Dissipation and Energy Retention Functions

The product of Φ with the temperature, T, is called the *energy dissipation function,*

$$\Psi = T\Phi = \frac{A}{V}v > 0, \tag*{$(22.7)_1$}$$

because it represents energy dissipated per unit volume and unit time. In any single chemical reaction the energy dissipation function is positive definite.

The negative inverse of the energy dissipation function,

$$\Upsilon = -\Psi < 0, \tag*{$(22.7)_2$}$$

will be called the *energy retention function.* Since the energy dissipated is taken as positive, Υ stands for a negative amount of energy. This is *retained* in that it is not dissipated and is negative definite in any single chemical reaction.

22.8 The Phenomenological Equation

Since the affinity, A, and the extent of reaction, ξ, are conjugate quantities, so are A and v. The rate of reaction, v, is clearly a function of A/T which is appropriately called the *driving force* of the reaction. If v depends linearly on A/T we have

$$v = L\,\frac{A}{T} \tag*{(22.8)}$$

where L is the *kinetic* or *phenomenological coefficient.* Equation (22.8) is termed the *phenomenological equation* of the reaction. To assign meaning to the phenomenological coefficient, L, we need to find a suitable *linear* relation between v and A/T.

22.9 Relation between the Rate of Reaction and its Driving Force

We seek a *general* expression linking v and A/T. The overall rate of reaction, v, is the difference between the forward rate, $\overrightarrow{v}$, and the backward rate, $\overleftarrow{v}$. It is shown in the theory of chemical kinetics that

$$\overrightarrow{v} = \overrightarrow{\mathrm{k}}\prod_{j=1}^{j=\mathrm{r}} \mathrm{c}_j^{|\nu_j|} \quad \text{and} \quad \overleftarrow{v} = \overleftarrow{\mathrm{k}}\prod_{j=\mathrm{r}+1}^{j=\mathrm{n}} \mathrm{c}_j^{|\nu_j|} \tag*{$(22.9)_1$}$$

where r is the number of reactants, n − r is the number of products, and $\overrightarrow{\mathrm{k}}$ and $\overleftarrow{\mathrm{k}}$ are called the kinetic constants. It is further shown in the kinetic theory that the ratio of the kinetic constants is equal to the equilibrium constant so that

$$\overrightarrow{\mathrm{k}}/\overleftarrow{\mathrm{k}} = \mathrm{K_c}(T)\,. \tag*{$(22.9)_2$}$$

We thus have

$$v = \overrightarrow{v} - \overleftarrow{v} = \overrightarrow{v}\left[1 - \frac{\overleftarrow{\mathrm{k}}\prod_{j=r+1}^{j=n} \mathrm{c}_j^{|\nu_j|}}{\overrightarrow{\mathrm{k}}\prod_{j=1}^{j=r} \mathrm{c}_j^{|\nu_j|}}\right] = \overrightarrow{v}\left[1 - \frac{\prod_{j=r+1}^{j=n} \mathrm{c}_j^{|\nu_j|}}{\mathrm{K_c}(T)\prod_{j=1}^{j=r} \mathrm{c}_j^{|\nu_j|}}\right]. \qquad (22.9)_3$$

But, since the ν_j's of the reactants carry the negative sign,

$$\prod_{j=1}^{j=n} \mathrm{c}_j^{\nu_j} = \prod_{j=r+1}^{j=n} \mathrm{c}_j^{|\nu_j|} \Big/ \prod_{j=1}^{j=r} \mathrm{c}^{|\nu_j|}, \qquad (22.9)_4$$

and we find

$$v = \overrightarrow{v}\left[1 - \frac{\prod_j \mathrm{c}_j^{\nu_j}}{\mathrm{K_c}(T)}\right] = \overrightarrow{v}\left[1 - \frac{\prod_j P_j^{\nu_j}}{\mathrm{K_P}(T)}\right], \qquad (22.9)_5,$$

where the second equation follows because

$$\mathrm{K_c}(T)\Big/\prod\nolimits_j \mathrm{c}_j^{\nu_j} = 1 = \mathrm{K_P}(T)\Big/\prod\nolimits_j P_j^{\nu_j} \qquad (22.9)_6$$

by Eqs.$(21.2)_7$ and $(21.3)_2$. Using Eq.$(21.2)_8$ we obtain

$$v = \overrightarrow{v}\left[1 - \exp\left(-\frac{A}{\mathrm{R}T}\right)\right] \qquad (22.9)_7$$

as the sought-for general relation between and v and A/T.

22.10 Dynamic Equilibrium – The Steady State

Equation$(22.9)_7$ is not a linear relation between v and A/T. However, as equilibrium is approached, A becomes quite small and the exponential may then be approximated by $1 - A/\mathrm{R}T$. At the same time, both the forward and the backward reaction rates approach the same value[21], the equilibrium rate, v_{eq}. Hence,

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[21] This is required by the principle of microscopic reversibility (cf. § 23.9).

$$\lim_{\overrightarrow{\nu} \to \overleftarrow{\nu} \to \nu_{\mathrm{eq}}} \nu = \frac{\nu_{\mathrm{eq}}}{\mathrm{R}} \frac{A}{T} . \qquad (22.10)_1$$

In this limit, therefore, a *dynamic equilibrium* or *steady state* will be reached in which the rate at which products are formed equals the rate at which reactants are reformed (microscopic reversibility, see § 23.9). We then regain Eq. (22.8) with L now given by

$$L = \nu_{\mathrm{eq}}/\mathrm{R} . \qquad (22.10)_2$$

Equation $(22.10)_2$ identifies the phenomenological coefficient, L, as the equilibrium rate of reaction divided by R, the universal gas constant. It is in the nature of chemical reactions that a linear phenomenological equation applies only quite close to equilibrium and that, hence, a meaningful interpretation of the phenomenological coefficient is possible only in that limit.

22.11 Scalar Steady-State Theory

We may now rewrite the phenomenological equation, Eq.(22.8), in the terminology of the theory of the steady state to be discussed more fully in the next Chapter. The equation then takes the form

$$J = LF \qquad (22.11)_1$$

where

$$J = \nu = \frac{d\xi}{dt} \qquad (22.11)_2$$

(i.e., the rate of reaction) is termed the *thermodynamic scalar flux*, and

$$F = \frac{A}{T} \qquad (22.11)_3$$

is called the *thermodynamic scalar driving force*.

Because the variables in Eq.(22.11) are all scalars, the thermodynamics of chemical reactions in dynamic equilibrium is called a scalar steady-state theory.

22.12 Simultaneous Reactions

In the preceding sections we were concerned with entropy production in a single reaction. If k reactions occur simultaneously (cf. § 21.10), rewriting $\mathrm{Eq.}(20.5)_2$ for the case of multiple reactions yields

$$A_{\mathrm{k}} = -\Sigma_j \mu_j \nu_{j\mathrm{k}} \qquad (22.12)_1$$

for the affinity of the *k*th reaction. By de Donder's inequality and the additivity of the entropy, the entropy production in the interior of the system is then given by

$$d_iS = \frac{1}{T}\sum\nolimits_k \nu_k A_k d\xi_k\,. \tag{22.12$_2$}$$

Hence, the rate of entropy production per unit volume, i.e., the entropy production function, results as

$$\Phi = \frac{1}{VT}\sum\nolimits_k \nu_k A_k\,, \tag{22.12$_3$}$$

and we obtain

$$\Upsilon = -T\Phi = -\frac{1}{V}\sum\nolimits_k \nu_k A_k\,. \tag{22.12$_4$}$$

for the energy retention function.

22.13 Coupled Reactions

When two reactions occur simultaneously, we have

$$\Phi = \frac{1}{VT}(A_1\nu_1 + A_2\nu_2) \tag{22.13}$$

for the entropy production function. It is perfectly possible to have two reactions occurring simultaneously for which $A_1\nu_1 < 0$ and $A_2\nu_2 > 0$, provided that $\Phi > 0$. Such reactions are called *coupled reactions*. They are of great importance in biological processes.

23. THE POSTULATES OF STEADY-STATE THERMODYNAMICS

Chapter 4 identified the problem of equilibrium as the central problem of the theory of equilibrium thermodynamics. The central problem of the thermodynamic theory of irreversible processes is the determination of the entropy produced as internally generated heat due to the various dissipative phenomena (cf. §§ 2.7, 2.18, 7.3 and 7.5) occurring in any natural spontaneous process. In the preceding chapter we have examined entropy production in chemical reactions. To determine the production of entropy in the general case is a rather difficult problem. No general theory of non-equilibrium thermodynamics is available. Much progress has been made, however, in the understanding of processes *near* equilibrium when the system is in a steady state, and when the steady state is characterized by linear relations between conjugate parameters. In most cases of practical interest the restriction to near equilibrium is not as stringent as it is in the case of chemical reactions. The remainder of this text is concerned primarily with the thermodynamics of the (linear) steady state.

23.0 Chapter Contents

23.1 The Postulatory Basis of Steady-State Thermodynamics

Development of a comprehensive theory of steady-state thermodynamics requires the introduction of three new postulates in addition to those of equilibrium thermodynamics. The first of these is the postulate of the existence of *local equilibrium*. The second establishes relations between *generalized thermodynamic driving forces* and *generalized thermodynamic fluxes*. The third postulate imposes *symmetry restrictions* on these relations.

23.2 Local Equilibrium – POSTULATE VI

Postulate VI states that:

> "*Although a thermodynamic system as a whole may not be in equilibrium, small elements of its volume may be considered to be in thermodynamic equilibrium locally. Elements in local equilibrium can be characterized by the same state functions that characterize global equilibrium in equilibrium thermodynamics.*"

It is this postulate that permits us to place steady-state thermodynamics firmly onto the basis formed by the five postulates of equilibrium thermodynamics.

23.3 The Steady State

In view of Postulate VI we refine our earlier definition of the steady state (§ 1.12) as follows:

> *"A steady, or stationary, state of a thermodynamic system is a stable, time-invariant state, generally of an open system, which is characterized by local equilibrium of the thermodynamic variables."*

The steady state is sustained by stable, time-invariant conditions at the system boundaries (see Appendix 7 for an example). These maintain a spontaneous, hence irreversible, process, resulting in the production of entropy.

23.4 Scalar Theory

In Chapter 22 we had already developed most of the basic concepts of the thermodynamics of the steady state when we considered chemical reactions as irreversible processes. We showed (cf. § 22.10) that in dynamic reaction equilibrium, i.e., in the steady state, the thermodynamic driving force, $F = A/T$, and the thermodynamic flux, $J = v$, could be related linearly through the phenomenological equation, $J = LF$ in which L is the phenomenological coefficient. The equation contains only scalar quantities. The theory of chemical reactions viewed as irreversible processes is, therefore, a *scalar theory*. That scalar theory is, however, easily extended to a general theory of coupled linear steady-state processes by considering F to be a *generalized* thermodynamic scalar driving force (or *generalized* thermodynamic scalar affinity), and J to be a *generalized* thermodynamic scalar flux.

23.5 Vector Theory

In many steady-state processes of interest, the thermodynamic fluxes and the driving forces that give rise to them are vector[22] quantities. The former are called *generalized thermodynamic vector fluxes, flows,* or *currents*, and will be represented by the symbols $\boldsymbol{J}$ or J_i. These flow vectors are typically the fluxes (quantity per unit time per unit volume) of the extensive parameters of a system, such as the internal energy or the entropy. The *generalized thermodynamic driving forces* or *generalized thermodynamic affinities* that elicit them will be represented by the symbols $\boldsymbol{F}$ or F_i. They are typically the gradients of a system's intensive parameters, exemplified by the temperature, pressure, or chemical potential. The fluxes and driving forces are *conjugate quantities.*

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[22] Scalars are set in non-bold italics (S). Vectors and tensors will be represented in the indicial as well as in the symbolic notation. In the indicial notation vectors and tensors are set in non-bold italics as are scalars. The number of indices (zero, one, or two) identify the variable as a scalar, a vector, or a (second-rank) tensor. In the symbolic notation, vectors are set in bold italic serif type ($\boldsymbol{V}$) while second rank tensor are set in bold italic sans-serif type ($\boldsymbol{\mathsf{F}}$). Thus, in the symbolic notation, vectors and tensors are in bold type but scalars are not. A single contraction, e.g., that of two vectors to a scalar, is indicated by a raised bold dot ($\boldsymbol{\cdot}$). A double contraction, e.g., that of two second-rank tensors to a scalar, is indicated by a bold colon (**:**).

This text describes steady-state thermodynamics primarily in terms of the vector theory.

23.6 Tensor Theory

The generalized thermodynamic driving forces and fluxes may also be second-order tensors typified by, e. g., stress, strain, and rate of strain tensors. Such tensors would be represented by the symbols $\boldsymbol{F}$ or F_{ij}, and $\boldsymbol{J}$ or J_{kl}. The tensor theory encompasses the vector theory as a special case, while the vector theory comprises the scalar theory in similar fashion. However, the tensor theory is beyond the scope of this text and will therefore receive only an occasional mention (cf. e.g., §§ 23.7, 26.1, and 26.2). Extension to tensors of rank higher than the second does not seem to be required in the theory of steady-state thermodynamics.

23.7 The Curie Symmetry Principle

In the general case the generalized fluxes of whatever tensorial character are functions of all the generalized thermodynamic forces. In a system which is isotropic at equilibrium, symmetry considerations restrict these functional dependencies. According to P. Curie (1908):

> *"Quantities whose tensorial characters differ by an odd number of ranks cannot interact in an isotropic medium."*

The principle can be understood as follows. If the thermodynamic forces and fluxes are tensors of the same rank, the elements of the matrix of phenomenological coefficients are scalars which depend on the local state of the medium but in an isotropic medium do not depend on the gradients of the intensive parameters. If they are tensors of different rank, the phenomenological coefficients are tensors of rank equal to the difference between the ranks of these tensors. A phenomenological coefficient which is a tensor of even rank can exist in an isotropic medium. One of odd rank would, however, cause the medium to be anisotropic and therefore cannot exist in an isotropic medium.

The Curie principle asserts the absence of cross-effects between scalar and vector phenomena in an isotropic medium. Second rank tensors can be separated into spherical and deviatoric tensors. The former can be treated as scalars. Cross-effects from the traceless deviatoric tensors appear to be weak or non-existent.

23.8 Phenomenological Equations – POSTULATE VII

The thermodynamic vector fluxes are linked to the driving forces through second-order tensors denoted by $\boldsymbol{L}$ or L_{ik}. The latter are the *generalized phenomenological coefficients, kinetic coefficients,* or *thermodynamic conductances* or *conductivities.* The interrelations among these quantities are the *phenomenological equations.*

Postulate VII states that:

> *"The generalized thermodynamic vector fluxes depend on all the generalized thermodynamic driving forces through the phenomenological coefficients."*

This is expressed succinctly by the equations

$$\boldsymbol{J} = \mathbf{L} \cdot \boldsymbol{F} \qquad \text{or} \qquad J_i = L_{ik} F_k \tag{23.8}$$

where the $\boldsymbol{J}$ or J_i are the vector fluxes, the $\boldsymbol{F}$ or F_k are the driving forces, and the $\mathbf{L}$ or L_{ik} are the phenomenological coefficients linking them. We note that the fluxes and forces are related linearly. Invoking a mechanical analogy, Eqs. (23.8) are also called the *thermodynamic equations of motion.*

23.9 Reciprocity Relations – POSTULATE VIII

Postulate VIII asserts that:

> *"The phenomenological coefficients are related by the Onsager reciprocity relations, $L_{ik} = L_{ki}$, if there are no forces determined by a vector product, and by $L_{ik}(\mathbf{f}) = L_{ki}(-\mathbf{f})$, the Onsager-Casimir reciprocity relations, if there are.*

The Onsager-Casimir relations apply in the presence of Coriolis forces (in a rotating system) or of Lorentz forces (in a system subjected to centrifugal or magnetic fields). The field vector, **f**, is thus either the angular velocity, ω, or the (external) magnetic field, **B**.

The statistical mechanical analog of the reciprocity relations is the *principle of microscopic reversibility.* As formulated by Tolman (1938), it states:

> *"Under equilibrium conditions any molecular process and the reverse of that process will take place on the average at the same rate."*

We had appealed to this principle earlier in § 22.10.

23.10 The Linear Steady State

The global equilibrium state is the limiting case of the steady state when the fluxes from the environment approach zero, i.e., when the system becomes isolated. If

- the phenomenological coefficients are *time-invariant* (Postulate VI),
- the phenomenological equations are *linear* (Postulate VII), and
- the matrix L_{ik} is *symmetrical* (Postulate VIII),

a steady state will be called a *linear steady state.*

24. COUPLED LINEAR STEADY STATES

Linear steady-state thermodynamics truly comes into its own when it considers spontaneous vector processes that are *coupled*, i.e., occur simultaneously and influence each other. Thus, that part of non-equilibrium thermodynamics which is the subject of this text might more appropriately be called the *thermodynamics of coupled linear steady states.* This chapter lays the groundwork for more detailed considerations to follow in subsequent chapters.

24.0 Chapter Contents

24.1 Parallel Concepts in Equilibrium and Steady-State Thermodynamics

It is useful to consider certain features in the thermodynamics of coupled linear steady states that parallel concepts in equilibrium thermodynamics. While they are not strict analogies, these correspondences do help in understanding the formal aspects of linear steady-state thermodynamics. Thus, as already asserted in § 23.5, the generalized thermodynamic vector fluxes, $\boldsymbol{J}$, of the steady-state theory are the time rates of change of the extensive parameters of the equilibrium theory, while the generalized thermodynamic vector driving forces, $\boldsymbol{F}$, are the gradients of the intensive parameters.

These corrspondences are brought into relief by comparing the energy and the entropy representations of the Euler equation of the equilibrium theory with the energy retention and entropy production functions of the steady-state theory. In thermal diffusion, where pressure-volume effects are absent, the Euler equation for the energy, Eq.(3.10)$_4$, is

$$U = TS + \sum_j \mu_j N_j \,, \qquad (24.1)_1$$

while that for the entropy, Eq.(3.10)$_5$, takes the form

$$S = \frac{1}{T} U - \sum_j \frac{\mu_j}{T} N_j \,. \qquad (24.1)_2$$

These equations are seen to parallel those of the energy retention function,

$$\Upsilon = \nabla T \cdot \boldsymbol{J}_S + \sum_j \nabla \mu_j \cdot \boldsymbol{J}_{N_j} \,, \qquad (24.1)_3$$

[cf. Eq.(27.3)$_4$], and the entropy production function,

$$\Phi = \nabla\left(\frac{1}{T}\right) \cdot J_U - \sum_j \nabla\left(\frac{\mu_j}{T}\right) \cdot J_{N_j} \qquad (24.1)_4$$

[cf. Eq.(27.2)$_4$] of the steady state theory. In these equations J_{N_j} is the flux of the jth matter species. The fluxes J_U, J_S and J_{N_j} will be derfined in the next chapter..

We recognize that—as asserted—the vector products of the gradients of the intensive parameters and the fluxes of the extensive parameters in the functions Υ and Φ parallel the scalar products of the intensive and extensive parameters in the equations for U and S of the equilibrium theory. For more on the subject of parallel concepts in the two theories see §§ 26.5, 26.6, 27.1, 27.4, and 28.8.

24.2 The Pivotal Functions of Linear Steady-State Thermodynamics

In view of the foregoing it should come as no surprise that in the thermodynamics of coupled linear systems the *entropy production function*, Φ, and the *energy retention function*, Υ, assume roles that are somewhat similar to those played by the cardinal functions, S, and U, of equilibrium thermodynamics. They assume a pivotal role in Part II of this text and will therefore be called the *pivotal functions* of the thermodynamics of the linear steady-state. They will be more fully discussed in Chapter 26 and in Sections 27.2 and 27.3.

24.3 Entropy Production and Energy Retention Representation

In Part I of this text we have made extensive use of the entropy and energy representations of the fundamental equation. In the thermodynamics of coupled linear steady states we employ the parallel concepts of the *entropy production* and *energy retention representations* to express the generalized fluxes and forces, the phenomenological equations and phenomenological coefficients, as well as the quantities of transport (cf. Chapter 28), in terms of one or the other of the two pivotal functions. Although different in form, the two representations are entirely equivalent (cf. § 28.8) just as the entropy and energy representations of equilibrium thermodynamics (cf. § 3.1).

24.4 The Phenomenological Equations in the Two Representations

In § 23.8 Postulate VII introduced the phenomenological equations $\boldsymbol{J} = \boldsymbol{L} \cdot \boldsymbol{F}$ where the $\boldsymbol{J}$ are the vector fluxes, the $\boldsymbol{F}$ are the vector driving forces, and the $\boldsymbol{L}$ are the second order tensors formed from the phenomenological coefficients in the *entropy production representation*. To distinguish between this and the energy retention representation we write $\boldsymbol{J} = \boldsymbol{\Lambda} \cdot \boldsymbol{Z}$, or $J_i = \Lambda_{ik} Z_k$, for the phenomenological equations in the *energy retention representation*, using the symbols Λ and Λ_{ik} for the phenomenological coefficients, and $\boldsymbol{Z}$ and Z_k for the vector driving forces.

24.5 Significance of the Phenomenological Coefficients

The phenomenological coefficients L_{ik} or Λ_{ik} in the phenomenological equations represent material properties. By the reciprocity relations introduced through Postulate VIII the matrices $[L_{ik}]$ and $[\Lambda_{ik}]$ are symmetrical, i.e., $L_{ik} = L_{ki}$, and $\Lambda_{ik} = \Lambda_{ki}$.

The cross-coefficients (the off-diagonal elements, $L_{ik(i \neq k)}$ or $\Lambda_{ik(i \neq k)}$) of the matrices may be zero. Thus, if $L_{ik(i \neq k)} = 0$, the thermodynamics of the linear steady-state provides the theoretical foundation for such well known empirical relations as Fourier's law of heat conduction (§ 27.9), Fick's first law of diffusion (§ 27.10), Ohm's law of electrical resistance, and others more.

In coupled processes the cross-coefficients are not zero. Their numerical values are identical but their physical interpretations differ.

24.6 Physical Interpretation of the Phenomenological Cross-Coefficients

The ikth phenomenological cross-coefficient in the entropy production representation is the partial derivative of the ith flux with respect to the kth driving force, i.e.,

$$L_{ik} = \left.\frac{\partial J_i}{\partial F_k}\right|_{x_n(n \neq k)} . \qquad (24.6)_1$$

It follows from the reciprocity relation, $L_{ik} = L_{ki}$, that

$$\left.\frac{\partial J_i}{\partial F_k}\right|_{F_n(n \neq k)} = \left.\frac{\partial J_k}{\partial F_i}\right|_{F_n(n \neq i)} . \qquad (24.6)_2$$

Thus an increase in the flux J_i elicited by unit increase in the driving force F_k when all other forces are held constant, is equal to an increase in the flux J_k elicited by unit increase in the driving force F_i.

In the energy retention representation we have analogously

$$\Lambda_{ik} = \left.\frac{\partial J_i}{\partial Z_k}\right|_{x_n(n \neq k)} \qquad (24.6)_3$$

and

$$\left.\frac{\partial J_i}{\partial Z_k}\right|_{Z_n(n \neq k)} = \left.\frac{\partial J_k}{\partial Z_i}\right|_{Z_n(n \neq i)} . \qquad (24.6)_4$$

Equations $(24.6)_2$ and $(24.6)_4$ exhibit formal analogies with the Maxwell relations of equilibrium thermodynamics [cf. Eq.$(A2.2)_{6.2}$].

24.7 Simultaneous Flow of Heat and Matter – Thermal Diffusion

In § 1.2 we defined thermodynamics as the science of heat as a special form of energy exchange. Non-equilibrium thermodynamics is therefore concerned with processes in which a heat flux is coupled with one or more other fluxes. Among these other fluxes a matter flux is probably didactically the most useful to discuss. The text will therefore concentrate on the steady-state thermodynamics of a simultaneous flow of heat and matter (i.e., *thermal diffusion*).

The simultaneous flow of heat and matter (see Chapters 25, 27, and 28) is characterized by two fluxes. In the *entropy production representation* the two fluxes are the energy flux, J_U, and the mass-action flux, J_M. In the *energy retention representation* the two fluxes are the entropy flux, J_S, and again the mass-action flux, J_M. The latter is defined in § 27.1. J_U and J_S appear in these formulations because, as has been pointed out in § 2.10, a matter flux always carries with it a certain amount of energy, and it also carries along entropy.

25. ENTROPY PRODUCTION IN THE STEADY STATE

The preceding chapter introduced the notion of the two pivotal functions of steady-state thermodynamics, the entropy production function, Φ, and the energy retention function, Υ, without as yet having addressed the underlying issue of the production of entropy in the steady state. This issue, as stated in the introduction to Chapter 23, is the basic problem of the thermodynamics of irreversible processes, and thus also of the thermodynamics of coupled linear steady states. In accordance with § 24.7 the present chapter therefore considers the rate at which entropy is produced in a simultaneous flow of matter and heat. To do this, we first establish the equations of continuity for the energy, for the matter, and for the entropy, in a region small enough to be in *local equilibrium* (Postulate VI). The continuity equation for the entropy yields the rate of entropy production per unit volume in the region. Integration over all regions then furnishes the global rate of entropy production, Θ. The entropy production function is then obtained simply by dividing Θ by the volume, V, since Φ is the rate at which entropy is produced per unit time and unit volume (cf. § 22.6).

25.0 Chapter Contents

25.1 The Gibbs Equation for Simultaneous Matter and Heat Flow

The starting point in our presentation of the steady-state thermodynamics of a simultaneous flow of matter and heat is the Gibbs equation, the differential form of the fundamental equation. Consider a system consisting of a fluid mixture contained in a vessel of fixed volume, V. The walls of the vessel are diathermal and permeable to the jth matter species. The Gibbs equation in the entropy representation, Eq.$(3.9)_2$,

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum\nolimits_j \frac{\mu_j}{T}dN_j \,, \qquad (25.1)_1$$

is reduced, in view of the fixed volume, to

$$ds = \frac{1}{T}du - \sum\nolimits_j \frac{\mu_j}{T}dc_j \qquad (25.1)_2$$

where $s = S/N$, $u = U/N$, and $c_j = N_j/N$.

In the energy representation the Gibbs equation becomes

$$du = Tds + \sum\nolimits_j \mu_j dc_j \,. \tag*{(25.1)$_3$}$$

Equations (25)$_2$ and (25.1)$_3$ are molar forms of the Gibbs equation (cf. § 14.3).

25.2 The Continuity Equation for the Energy

We now establish the equation of continuity for the energy. Let R be a region within the vessel with volume, ϕ, and surface, σ. We consider this volume to be small enough so that it is in *local equilibrium* (Postulate VI). If dv is an elemental volume in R, the total internal energy in the region is $\int_\phi u\ du$. The rate at which the internal energy changes in the region R equals the rate at which energy enters or leaves R across its surface, σ. Introducing the *energy flux, energy flow vector,* or *energy current density,* J_U, as the amount of energy crossing unit area in unit time, we have

$$-\int_\phi \frac{du}{dt} dv = \int_\sigma \boldsymbol{J}_U \cdot \boldsymbol{da} \tag*{(25.2)$_1$}$$

where $\boldsymbol{da}$ is an elemental vector area of the surface, σ, and the flow vector is defined as positive for *outward* flow. Thus, Eq.(25.2)$_1$ expresses the fact that the energy within the region R decreases when the matter flows from the inside to the outside of the region. Now, by the divergence theorem,

$$\int_\sigma \boldsymbol{J}_U \cdot \boldsymbol{da} = \int_\phi \nabla \cdot \boldsymbol{J}_U \, dv \,, \tag*{(25.2)$_2$}$$

and, therefore,

$$\int_\phi \left(\frac{du}{dt} + \nabla \cdot \boldsymbol{J}_U \right) dv = 0 \,. \tag*{(25.2)$_3$}$$

But this is true for an arbitrary volume, dv. Consequently, the continuity equation for the energy becomes

$$\frac{du}{dt} + \nabla \cdot \boldsymbol{J}_U = 0 \,. \tag*{(25.2)$_4$}$$

The first term on the left represents the increase in the energy in the region R per unit time. The second term represents the rate of outflow of the energy from the region per unit area of surface in an exchange with the surroundings. According to Eq.$(25.2)_4$ the sum of the two terms is zero. The equation thus expresses the *conservation of energy* (cf. § 2.4).

25.3 The Continuity Equation for the Matter

The amount of the jth species of matter in R is $\int_\phi c_j\,dv$. We introduce the *matter flux, matter flow vector,* or *matter current density,* $\boldsymbol{J}_{N_j}$, of the jth species as the number of moles of j, N_j, entering or leaving R across unit area of its surface, σ, in unit time. Here also, the flow vector is defined as positive for *outward* flow. Hence, we have

$$-\int_\phi \frac{dc_j}{dt}\,dv = \int_\sigma \boldsymbol{J}_{N_j}\cdot d\boldsymbol{a}\,. \tag*{$(25.3)_1$}$$

Again invoking the divergence theorem, the continuity equation for the jth species of matter results as

$$\frac{dc_j}{dt} + \nabla\cdot\boldsymbol{J}_{N_j} = 0\,. \tag*{$(25.3)_2$}$$

The first term on the left represents the increase in the matter contained in the region R per unit time. The second term represents the rate of outflow of matter from the region per unit area of surface in an exchange with the surroundings. By Eq.$(25.3)_2$ the sum of the two terms is zero. The equation thus expresses the *conservation of matter.*

25.4 The Continuity Equation for the Entropy

We are now ready to calculate the local rate of change of the entropy, i.e., the rate of entropy production in the local region R. By Eq.$(25.1)_2$

$$\frac{ds}{dt} = \frac{du}{Tdt} - \sum\nolimits_j \frac{\mu_j dc_j}{Tdt}\,. \tag*{$(25.4)_1$}$$

Substituting from Eqs. $(25.2)_4$ and $(25.3)_2$ gives

$$\frac{ds}{dt} = -\frac{1}{T}\nabla\cdot\boldsymbol{J}_U + \sum\nolimits_j \frac{\mu_j}{T}\nabla\cdot\boldsymbol{J}_{N_j}\,. \tag*{$(25.4)_2$}$$

But, if λ is a scalar, and $\mathbf{A}$ is a vector, then

$$\lambda\nabla\cdot\mathbf{A} = \nabla\cdot(\lambda\mathbf{A}) - \mathbf{A}\cdot\nabla\lambda\,. \tag*{$(25.4)_3$}$$

Making use of this identity in both terms on the right hand side of Eq.$(25.4)_2$, and introducing the *entropy flux, entropy flow vector,* or *entropy current density,*

$$J_S = \frac{1}{T} J_U - \sum\nolimits_j \frac{\mu_j}{T} J_{N_j} \tag{25.4$_4$}$$

we obtain

$$\frac{ds}{dt} + \nabla \cdot J_S = \nabla\left(\frac{1}{T}\right) \cdot J_U - \sum\nolimits_j \nabla\left(\frac{\mu_j}{T}\right) \cdot J_{N_j} \,. \tag{25.4$_5$}$$

This equation is the equation of continuity for the entropy in the region R. The first term on the left represents the increase of the entropy per unit time. The second term represents the rate of outflow of the entropy per unit area of surface in an exchange with the surroundings. The sum of these two terms is not zero. Hence, the entropy in the region R is not conserved. The right hand side represents the rate of production, generation, or creation of entropy in the region R per unit volume in unit time, i.e., the entropy production function, Φ. We thus have

$$\frac{ds}{dt} + \nabla \cdot J_S = \Phi \tag{25.4$_6$}$$

where

$$\Phi = \nabla\left(\frac{1}{T}\right) \cdot J_U - \sum\nolimits_j \nabla\left(\frac{\mu_j}{T}\right) \cdot J_{N_j} \tag{25.4$_7$}$$

is the entropy produced per unit time and unit volume. Since this does not vanish, Eq.(25.4)$_6$ expresses the *non-conservation of the entropy* {cf. § 2.17).

25.5 The Rate of Entropy Production

So far we have examined the situation in a region R of the total volume making use of the postulate of local equilibrium (Postulate VI). The *global* relations are obtained simply by integrating over all regions. Integrating Eq.(25.4)$_5$ over unit volume, V, and using the divergence theorem, we find

$$\frac{\mathrm{d}}{dt}\int_{\mathrm{V}} s\, dv + \int_{\Sigma} J_S \cdot \mathbf{da} = \int_{\mathrm{V}} \Phi\, dv = \Theta \,. \tag{25.5}$$

The right hand side of this equation is the *rate of entropy production*, Θ. If the vessel is isolated, the second integral on the left hand side vanishes. The first integral is thus seen to represent the entropy generated *within* the vessel per unit time, $d_i S/dt$. By Eq.(25.4)$_5$ this vanishes when the gradients of the temperature and of the chemical potentials vanish, i.e., at equilibrium.

26. THE PIVOTAL FUNCTIONS

Section 24.2 referred to the entropy production function, Φ, and the energy retention function, Υ, as the pivotal functions of the theory of coupled linear steady-state thermodynamics. These functions had first been introduced in §§ 22.6 and 22.7 in the framework of the scalar theory. We now extend their definition and meaning in some generality to the vector and tensor theories and elaborate some of their salient features.

26.0 Chapter Contents

26.1 The Entropy Production Function

The entropy production function is the sum of the products of the thermodynamic fluxes and their conjugate driving forces. If tensorial cross-effects are negligible, the Curie symmetry principle allows us to extend our earlier definition of the entropy production function, Φ, as one of the two pivotal functions of steady-state thermodynamics to include scalar, vector, and tensor quantities alike. In the most general case, then, the *entropy production function* becomes

$$\Phi = \sum\nolimits_{\mathrm{s}} F_{\mathrm{s}} J_{\mathrm{s}} + \sum\nolimits_{\mathrm{v}} \boldsymbol{F}_{\mathrm{v}} \cdot \boldsymbol{J}_{\mathrm{v}} + \sum\nolimits_{\mathrm{t}} \boldsymbol{\mathsf{F}}_{\mathrm{t}} : \boldsymbol{\mathsf{J}}_{\mathrm{t}} > 0 \tag*{$(26.1)_1$}$$

where the subscripts s, v, and t refer to the number of scalar, vector, and tensor pairs of variables. We shall call F, $\boldsymbol{F}$, and $\boldsymbol{\mathsf{F}}$ the thermodynamic driving forces in the entropy production representation. The entropy production function, Φ, is positive definite quantity (cf. § 22.6)..

Equation $(26.1)_1$ represents the most general case. When considering vector processes only, the entropy production function becomes simply

$$\Phi = \sum\nolimits_{\mathrm{v}} \boldsymbol{F}_{\mathrm{v}} \cdot \boldsymbol{J}_{\mathrm{v}} > 0 \tag*{$(26.1)_2$}$$

where the thermodynamic flow vectors, $\boldsymbol{J}_{\mathrm{v}}$, are the fluxes of the appropriate *extensive* parameters, while the vector driving forces, $\boldsymbol{F}_{\mathrm{v}}$, are the gradients, ∇I_{v}, of the conjugate *intensive* parameters in the entropy representation.

26.2 The Energy Retention Function

In equilibrium thermodynamics the relation $I_k = -Y_k/T$ [cf. Eq.(3.5)$_2$] links the intensive parameters of the physical work and mass action terms in the entropy representation to those in the energy representation. In linear steady-state theory we may similarly let

$$F_s = -Z_s/T, \qquad \boldsymbol{F}_v = -\boldsymbol{Z}_v/T, \qquad \mathbf{F}_t = -\mathbf{Z}_t/T. \tag{26.2)$_1$}$$

Introducing these relations into Eq.(26.1)$_1$, multiplying by T, and taking the negative inverse, we obtain the most general form of the *energy retention function as*

$$\Upsilon = -T\Phi = \sum\nolimits_s Z_s J_s + \sum\nolimits_v \boldsymbol{Z}_v \cdot \boldsymbol{J}_v + \sum\nolimits_t \mathbf{Z}_t : \mathbf{J}_t < 0, \tag{26.2)$_2$}$$

where the subscripts s, v, and t again refer to the number of scalar, vector, and tensor pairs of variables. The driving forces, Z, $\boldsymbol{Z}$, and $\mathbf{Z}$, will be called the thermodynamic driving forces in the energy retention representation. The energy retention function, Υ, is negative definite quantity (cf. § 22.7).

When considering vector processes only, the energy retention function becomes

$$\Upsilon = \sum\nolimits_v \boldsymbol{Z}_v \cdot \boldsymbol{J}_v < 0. \tag{26.2)$_3$}$$

In this function the thermodynamic flow vectors, $\boldsymbol{J}_v$, are again the fluxes of the appropriate *extensive* parameters while the vector forces, $\boldsymbol{Z}_v$, are the gradients of the conjugate *intensive* parameters in the energy representation, ∇Y_v.

26.3 The Energy Dissipation Function

The negative inverse of the general form of the energy retention function

$$\Psi = -\Upsilon = -\sum\nolimits_s Z_s J_s - \sum\nolimits_v \boldsymbol{Z}_v \cdot \boldsymbol{J}_v - \sum\nolimits_t \mathbf{Z}_t : \mathbf{J}_t > 0. \tag{26.3}$$

yields the general form of the *energy dissipation function,* or just the *dissipation function.* This function has the same dimensions as the energy retention function and is positive definite (cf. § 22.7)..

26.4 Determination of the Amount of Entropy Produced, or Energy Retained or Dissipated

It is one of the noteworthy features of the linear steady state that in this state, Φ, the amount of entropy produced, as well as Υ or Ψ, the amount of energy retained or dissipated per unit volume in unit time, can be calculated from the equations listed in §§ 26.1 and 26.2 if the fluxes and driving forces are measured.

26.5 Conjugate Generalized Fluxes and Driving Forces

As is obvious from Eq.(26.1)$_1$, the scalar products of J_s and F_s, the contractions of $\boldsymbol{J}_v$ and $\boldsymbol{F}_v$, and the double contractions of $\boldsymbol{J}_t$ and $\boldsymbol{F}_t$ have the dimensions (entropy per unit time and unit volume) of Φ, the entropy production function. They therefore constitute *conjugate* pairs of variables just like the parameters I_j and X_j in the entropy representation.

Similarly, by Eq.(26.2)$_2$, the scalar products of J_s and Z_s, the contractions of $\boldsymbol{J}_v$ and $\boldsymbol{Z}_v$, and the double contractions of $\boldsymbol{J}_t$ and $\boldsymbol{Z}_t$ have the dimensions (energy per unit time and unit volume) of Υ, the energy retention function. They thus also form *conjugate* pairs of variables as do the parameters Y_j and X_j in the energy representation.

26.6 Non-Uniqueness of the Entropy Production and Energy Retention Functions

Neither the entropy production function, nor the energy retention function are determined uniquely. It suffices that the products of whatever are chosen as the generalized fluxes and driving forces have the dimensions of *entropy* per unit time per unit volume [Φ], and *energy* per unit time per unit volume [Υ], respectively.

In dealing with vector fluxes and driving forces we thus must have

$$\Phi = \sum\nolimits_v \boldsymbol{J}_v \cdot \boldsymbol{F}_v = \sum\nolimits_v \boldsymbol{J}'_v \cdot \boldsymbol{F}'_v \qquad (26.6)_1$$

and

$$\Upsilon = \sum\nolimits_v \boldsymbol{J}_v \cdot \boldsymbol{Z}_v = \sum\nolimits_v \boldsymbol{J}'_v \cdot \boldsymbol{Z}'_v \qquad (26.6)_2$$

where the $\boldsymbol{J}'_v$ and $\boldsymbol{F}'_v$, and the $\boldsymbol{J}'_v$ and $\boldsymbol{Z}'_v$ are alternative pairs of conjugate vector fluxes and driving forces.

26.7 Transformation of Vector Fluxes and Driving Forces

It is often desirable to select an alternative pair of vector fluxes and driving forces. Examples of this occur in §§ 28.7 and 28.9. A transformation of fluxes will usually take the form

$$\boldsymbol{J}'_1 = \boldsymbol{J}_1 - I\,\boldsymbol{J}_2 \qquad \text{and} \qquad \boldsymbol{J}'_2 = \boldsymbol{J}_2 \qquad (26.7)_1$$

where I is an intensive variable such as, e.g., T, P, μ, or u, h, etc. The variable I must be chosen so that the equations are dimensionally correct.

Because of the constraint imposed by Eq.(26.6)$_1$, these transformations require that the driving forces in the entropy production representation become

$$\boldsymbol{F}'_1 = \boldsymbol{F}_1 \qquad \text{and} \qquad \boldsymbol{F}'_2 = \boldsymbol{F}_2 + I\,\boldsymbol{F}_1 \qquad (26.7)_2$$

when the fluxes and driving forces are selected as products of Φ. When they are chosen as products of Υ, the driving forces in the energy retention representation must take the form

$$\boldsymbol{Z}_1' = \boldsymbol{Z}_1 \qquad \text{and} \qquad \boldsymbol{Z}_2' = \boldsymbol{Z}_2 + I\,\boldsymbol{Z}_1 \qquad (26.7)_3$$

because of the constraint imposed now by Eq.$(26.6)_2$.

The same equations can be used for the transformation of the driving forces. We then start either from Eq.$(26.7)_2$ or from Eq.$(26.7)_3$, and require Eq.$(26.6)_2$.

26.8 Comparison between the Pivotal and the Cardinal Functions

In § 24.1 we compared the pivotal functions of the linear steady-state theory with the cardinal functions of the equilibrium theory. We now amplify this comparison.

Equation $(26.1)_2$,

$$\Phi = \sum_j \boldsymbol{F}_j \cdot \boldsymbol{J}_j\,, \qquad (26.8)_1$$

the entropy production function, Φ, may be compared with Eq.$(3.10)_3$, the entropy function,

$$S = \sum_j I_j X_j\,. \qquad (26.8)_2$$

In like manner, Eq.$(26.2)_3$,

$$\Upsilon = \sum_j \boldsymbol{Z}_j \cdot \boldsymbol{J}_j\,, \qquad (26.8)_3$$

for the energy retention function, Υ, bears comparison with Eq.$(3.10)_3$, the energy function,

$$U = \sum_j Y_j X_j\,. \qquad (26.8)_4$$

Clearly, the pivotal functions and the cardinal functions are formally analogous in that Φ and S, and Υ and U, both consist of the algebraic sums of the products of pairs of conjugate variables. In equilibrium thermodynamics S is the sum of products of the intensive parameters I and the extensive parameters X while U is the sum of products of the intensive parameters Y and again the extensive parameters X. In steady-state thermodynamics Φ is the sum of products of the generalized forces F, $\boldsymbol{F}$, and **F** and the generalized fluxes J, $\boldsymbol{J}$, and **J** while Υ is the sum of products of the generalized forces Z, $\boldsymbol{Z}$, and **Z** and again the generalized fluxes J, $\boldsymbol{J}$, and **J**. We note, however, that while S and U are themselves extensive parameters, Φ and Υ are *not* generalized fluxes, and neither are they equations of state.

Furthermore, while the pairs of conjugate extensive and intensive parameters that compose the cardinal functions are unique, the pairs of conjugate generalized fluxes and generalized driving forces are not. Herein lies another difference between the energy and entropy representations of equilibrium thermodynamics, and the energy retention and entropy production representation of steady-state thermodynamics.

27. MATTER AND HEAT FLOW

In § 24.1 we had already presented the expressions for the pivotal functions, the entropy production function, Φ, and the energy retention function, Υ, in a simultaneous flow of matter and of heat at constant volume, i.e., in *thermal diffusion* (§ 24.7) without formally deriving them. We now proceed to do just that. This requires first of all the introduction of two new vectors, the first expressing the heat flux, the second the mass-action flux. We then establish the phenomenological equations in simultaneous heat and matter flow and define the Dufour and the Soret effects from the phenomenological cross coefficients. Finally, we relate the heat flux to Fourier's Law of Heat Conduction, and the mass-action flux to Fick's First Law of Diffusion.

27.0 Chapter Contents

27.1 Heat Flux and Mass-Action Flux

We introduce the *heat flux, heat flow vector,* or *heat current density,* J_Q, through the equation

$$J_Q = TJ_S \qquad (27.1)_1$$

where J_S is the entropy flux introduced in § 25.4.

We analogously define a *mass-action flux, mass-action flow vector,* or *mass-action current density,*

$$J_M = \sum\nolimits_j \mu_j J_{N_j} \qquad (27.1)_2$$

where J_{N_j} is the matter flux introduced in § 25.3.

The energy flux, J_U, then follows as

$$J_U = J_Q + J_M = TJ_S + \sum\nolimits_j \mu_j J_{N_j}. \tag{27.1$_3$}$$

This equation can be viewed in the light of Eq.(2.6)$_1$ which expresses the conservation of energy in equilibrium thermodynamics. At constant volume the work term in that equation is zero and the equation becomes

$$\Delta U = Q + M = T\Delta S + \sum\nolimits_j \mu_j \Delta N_j. \tag{27.1$_4$}$$

Comparison of the last two equations shows that the fluxes J_U, J_Q, and J_M may be viewed in some sense as the steady-state equivalents of the equilibrium quantities ΔU, Q, and M.

27.2 The Entropy Production Function in Simultaneous Matter and Heat Flow

In simultaneous matter and heat flow the entropy production function, Φ, is characterized by the energy flux, J_U, and the mass-action flux, J_M (cf. § 27.1). It is therefore given by

$$\Phi = F_U \cdot J_U + F_M \cdot J_M = F_U \cdot J_U + \sum\nolimits_j F_{N_j} \cdot J_{N_j} \tag{27.2$_1$}$$

where

$$F_U = \nabla\left(\frac{1}{T}\right) \tag{27.2$_2$}$$

is the driving force for the energy flux, while F_M is the driving force for the mass-action flux, both forces being formulated in the entropy production representation. For the latter flux we have $J_M = \sum_j \mu_j J_{N_j}$, and thus $F_M = \sum_j F_{N_j}$, where J_{N_j} is the flux of the jth species of matter, driven by

$$F_{N_j} = -\nabla\left(\frac{\mu_j}{T}\right). \tag{27.2$_3$}$$

We thus have

$$\Phi = \nabla\left(\frac{1}{T}\right) \cdot J_U - \sum\nolimits_j \nabla\left(\frac{\mu_j}{T}\right) \cdot J_{N_j} \tag{27.2$_4$}$$

which should be compared with Eq.(25.4)$_7$.

The driving forces in the entropy production representation, F_U, the *thermal driving force*, and F_{N_j}, the *jth diffusional driving force*, are recognized as the gradients of the intensive parameters in the entropy representation. We see Eq.(27.2)$_1$ as a particular instance of Eq.(26.1)$_2$.

27.3 The Energy Retention Function in Simultaneous Matter and Heat Flow

In simultaneous matter and heat flow the energy retention function, Υ, is a function of the entropy flux, $\boldsymbol{J}_S$, and the mass-action flux, $\boldsymbol{J}_M$ (cf. § 27.1). It is thus given by

$$\Upsilon = \boldsymbol{Z}_S \cdot \boldsymbol{J}_S + \boldsymbol{Z}_M \cdot \boldsymbol{J}_M = \boldsymbol{Z}_S \cdot \boldsymbol{J}_S + \sum\nolimits_j \boldsymbol{Z}_{N_j} \cdot \boldsymbol{J}_{N_j} \tag*{(27.3)$_1$}$$

where

$$\boldsymbol{Z}_S = \nabla T \tag*{(27.3)$_2$}$$

is the driving force for the entropy flux, while $\boldsymbol{Z}_M$ is the driving force for the mass-action flux, both these forces being formulated in the energy retention representation. The latter flux, $\boldsymbol{J}_M$, is still the same, and we now have $\boldsymbol{Z}_M = \sum_j \boldsymbol{Z}_{N_j}$ where $\boldsymbol{J}_{N_j}$, the flux of the jth species of matter, is driven by

$$\boldsymbol{Z}_{N_j} = \nabla \mu_j \,. \tag*{(27.3)$_3$}$$

Thus we finally have

$$\Upsilon = \nabla T \cdot \boldsymbol{J}_S + \sum\nolimits_j \nabla \mu_j \cdot \boldsymbol{J}_{N_j} \,. \tag*{(27.3)$_4$}$$

The two driving forces in the energy retention representation, the *thermal driving force*, $\boldsymbol{Z}_S$, and the *jth diffusional driving force*, $\boldsymbol{Z}_{N_j}$, are recognized as the gradients of the intensive parameters in the energy representation. We recognize Eq.(27.3)$_1$ as a particular instance of Eq.(26.2)$_3$.

27.4 Relation between the Entropy Production and the Energy Retention Function

The relation between the entropy production function and the energy retention function follows from Eqs.(26.2)$_2$ as

$$\Upsilon = -T\Phi \,. \tag*{(27.4)$_1$}$$

To formally derive this relation we apply Eq.(27.4)$_1$ to the case of the simultaneous flow of heat and—for simplicity and without loss of generality—the flow of a single species of matter. By Eqs.(27.2)$_1$ and (27.3)$_1$ we then have

$$\Phi = \boldsymbol{F}_U \cdot \boldsymbol{J}_U + \boldsymbol{F}_N \cdot \boldsymbol{J}_N \tag*{(27.4)$_2$}$$

and

$$\Upsilon = \boldsymbol{Z}_S \cdot \boldsymbol{J}_S + \boldsymbol{Z}_N \cdot \boldsymbol{J}_N \,. \tag*{(27.4)$_3$}$$

But

$$\boldsymbol{F}_U = \nabla\left(\frac{1}{T}\right) = -\frac{1}{T^2}\nabla T \tag{27.4)$_4$}$$

while

$$\boldsymbol{F}_N = -\nabla\left(\frac{\mu}{T}\right) = -\frac{1}{T}\nabla\mu + \frac{\mu}{T^2}\nabla T \tag{27.4)$_5$}$$

and therefore

$$\Phi = -\frac{1}{T^2}\nabla T\cdot\boldsymbol{J}_U - \frac{1}{T}\nabla\mu\cdot\boldsymbol{J}_N + \frac{\mu}{T^2}\nabla T\cdot\boldsymbol{J}_N\,. \tag{27.4)$_6$}$$

Substitution of Eq.(27.1)$_3$, that is, $\boldsymbol{J}_U = T\boldsymbol{J}_S + \mu\boldsymbol{J}_N$, then yields

$$\Phi = -\frac{1}{T}\nabla T\cdot\boldsymbol{J}_S - \frac{1}{T}\nabla\mu\cdot\boldsymbol{J}_N\,, \tag{27.4)$_7$}$$

and application of Eq.(27.4)$_1$ leads to

$$\Upsilon = -T\Phi = \nabla T\cdot\boldsymbol{J}_S + \nabla\mu\cdot\boldsymbol{J}_N\,. \tag{27.4)$_8$}$$

But this is Eq.(27.4)$_3$ since $\nabla T = \boldsymbol{Z}_S$ and $\nabla\mu = \boldsymbol{Z}_N$.

We remark that the relation $\Upsilon = -T\Phi$ between the two pivotal functions parallels the relation $U = -TS$ between the cardinal functions [cf. Eq.(3.10)$_6$].

27.5 The Phenomenological Equations in the Entropy Production Representation

The simultaneous flow of matter and heat is a typical instance of the occurrence of two coupled processes. Accordingly, the phenomenological equations enjoined by Postulate VII contain cross-coefficients between the heat flux and the matter flux. Since in the *entropy production representation* the two fluxes are the *energy flux*, $\boldsymbol{J}_U$, and the mass-action flux, $\boldsymbol{J}_M$, the phenomenological equations take the form

$$\boldsymbol{J}_U = \boldsymbol{L}_{UU}\boldsymbol{F}_U + \sum\nolimits_k \boldsymbol{L}_{UN_k}\boldsymbol{F}_{N_k} \tag{27.5)$_1$}$$

for the former, and

$$\boldsymbol{J}_M = \sum\nolimits_j\left(\boldsymbol{L}_{N_jU}\boldsymbol{F}_U + \sum\nolimits_k \boldsymbol{L}_{N_jN_k}\boldsymbol{F}_{N_k}\right) \tag{27.5)$_2$}$$

for the latter. Equation (27.5)$_1$ expresses the energy flux as the sum of the energy transported as heat (a pure heat flow) and the energy transported by the diffusing particles of the fluid (a pure matter flow). Energy depends on temperature. Hence, in Eq.$(27.5)_2$, the matter flux depends on the thermal as well as the diffusional driving force.

27.6 The Phenomenological Equations in the Energy Retention Representation

In the *energy retention representation* of a simultaneous matter and heat flow the energy flux is replaced by the entropy flux,

$$J_S = \Lambda_{SS} \boldsymbol{Z}_S + \sum\nolimits_k \Lambda_{SN_k} \boldsymbol{Z}_{N_k} \,, \qquad (27.6)_1$$

and the mass-action flux becomes

$$J_M = \sum\nolimits_j (\Lambda_{N_jS} \boldsymbol{Z}_S + \sum\nolimits_k \Lambda_{N_jN_k} \boldsymbol{Z}_{N_k}) \,. \qquad (27.6)_2$$

In analogy to Eq.$(27.5)_1$, Eq.$(27.6)_1$ expresses the entropy flow as the sum of the entropies associated with the flow of heat and with the diffusion of the particles of the fluid. Similarly, Eq.$(27.6)_2$ shows that the matter flux again depends on the thermal as well as the diffusional driving force.

27.7 The Phenomenological Coefficients in Simultaneous Matter and Heat Flow – The Dufour and Soret Effects

In a simultaneous flow of matter and heat it is the cross-coefficients that are of interest. In the entropy production representation the cross-coefficient L_{UN_j} represents the tendency of the jth diffusional driving force, $\boldsymbol{F}_{N_j}$, to give rise to a flow of energy and is referred to as the *Dufour effect.* Its twin, L_{N_jU}, represents the tendency of the thermal driving force, $\boldsymbol{F}_U$, to give rise to a flow of the jth species of matter and is called the *Soret effect* or the *thermal diffusion effect.*

Similarly, in the energy retention representation Λ_{SN_j} represents the tendency of the jth chemical potential gradient, $\boldsymbol{Z}_{N_j}$, to give rise to an entropy flux, while Λ_{N_jS} represents the tendency of the temperature gradient, $\boldsymbol{Z}_S$, to give rise to a flow of the jth species of matter.

By Postulate VIII, $L_{UN_j} = L_{N_jU}$ and $\Lambda_{SN_j} = \Lambda_{N_jS}$. The reciprocity relations assert that the intensities of both tendencies are identical.

27.8 The Phenomenological Coefficients in Pure Heat and Pure Matter Flow

Let us now focus attention on L_{UU} and $L_{N_jN_j}$, the two same-index coefficients in the entropy production representation. In the absence of matter flow (i.e., when the chemical potential gradients vanish), Eq.$(27.2)_1$ becomes

$$\Phi = \boldsymbol{F}_U \cdot \boldsymbol{J}_U = \boldsymbol{F}_Q \cdot \boldsymbol{J}_Q \,. \qquad (27.8)_1$$

The entropy production is then seen to be the result of a pure heat flow, $\boldsymbol{J}_Q$, driven by $\boldsymbol{F}_Q$, the thermal driving force.

On the other hand, when the temperature gradient vanishes (i.e., at constant temperature), we find

$$\Phi = \boldsymbol{F}_U \cdot \boldsymbol{J}_U = \boldsymbol{F}_M \cdot \boldsymbol{J}_M = \sum\nolimits_j \boldsymbol{F}_{N_j} \cdot \boldsymbol{J}_{N_j} \ . \qquad (27.8)_2$$

In that case the entropy production is seen to result from $\boldsymbol{J}_M = \sum_j \boldsymbol{J}_{N_j}$, i.e., from a pure matter flow (diffusion).

We now proceed to analyze the meaning of first $\boldsymbol{L}_{UU}$, and then $\boldsymbol{L}_{N_jN_j}$.

27.9 Fourier's Law of Heat Conduction

For a pure heat flow the second term in Eq.(27.5)$_1$ vanishes and the phenomenological equation for the pure heat flow in the entropy production representation may be written as

$$\boldsymbol{J}_Q = \boldsymbol{L}_{QQ}\boldsymbol{F}_Q = \boldsymbol{L}_{QQ}\nabla\left(\frac{1}{T}\right) = -\frac{\boldsymbol{L}_{QQ}}{T^2}\nabla T \qquad (27.9)_1$$

where we have let $\boldsymbol{L}_{UU} = \boldsymbol{L}_{QQ}$. Comparing this with the empirical relation known as *Fourier's law of heat conduction*

$$\boldsymbol{J}_Q = -\kappa \nabla T \, , \qquad (27.9)_2$$

we see immediately that

$$\boldsymbol{L}_{QQ} = \kappa T^2 . \qquad (27.9)_3$$

This relates the phenomenological coefficient $\boldsymbol{L}_{QQ}$ to the material property κ known as the *thermal conductivity.*

27.10 Fick's First Law of Diffusion

Just as the phenomenological coefficient $\boldsymbol{L}_{QQ}$ can be related to the thermal conductivity, the phenomenological coefficient $\boldsymbol{L}_{N_jN_j}$ can be related to the material property known as the *coefficient of diffusion.*

The phenomenological equation for a pure matter flow of the jth species of matter is

$$\boldsymbol{J}_{N_j} = \boldsymbol{L}_{N_jN_j}\boldsymbol{F}_{N_j} = -\frac{\boldsymbol{L}_{N_jN_j}}{T}\nabla\mu_j \, . \qquad (27.10)_1$$

The second equation follows from Eq.(27.2)$_3$ because T is constant. Introducing the concentration of the jth species, c_j, we find

$$J_{N_j} = -\frac{L_{N_jN_j}}{T}\frac{\partial \mu_j}{\partial c_j}\bigg|_{T,P} \nabla c_j . \tag{27.10)$_2$}$$

Now, by Eq.(14.7)

$$\mu_j = \mu_j^*(T, \mathrm{P}) - \mathrm{R}T \, ln\, c + \mathrm{R}T \, ln\, c_j , \tag{27.10)$_3$}$$

since $\overline{n}_j = c_j/c$ where c is the total concentration. Thus, at constant c,

$$\frac{\partial \mu_j}{\partial c_j}\bigg|_{T,\mathrm{P}} = \frac{\mathrm{R}T}{c_j} , \tag{27.10)$_4$}$$

and, therefore,

$$J_{N_j} = -\frac{L_{N_jN_j}\mathrm{R}}{c_j}\nabla c_j . \tag{27.10)$_5$}$$

We can now give meaning to the phenomenological coefficient $L_{N_jN_j}$ in terms of the empirical relation known as *Fick's first law of diffusion*

$$J_{N_j} = -\mathrm{D}_j \nabla c_j . \tag{27.10)$_6$}$$

Comparing the last two equations we see immediately that

$$L_{N_jN_j} = \mathrm{D}_j c_j/\mathrm{R} . \tag{27.10)$_7$}$$

This expression relates the jth phenomenological coefficient to the material property known as the *diffusion coefficient*, D_j, of the jth species of matter.

28. THE QUANTITIES OF TRANSPORT

Chapter 27 discussed simultaneous matter and heat flow. We now examine a particular case of such a flow, the case of thermal migration through a barrier. This will lead us to recognize three specifically non-equilibrium quantities called *quantities of transport.* They are: the *entropy of transport*, the *energy of transport,* and the *heat of transport.* The latter is a true thermodynamic quantity which can be determined by calorimetric measurements in steady-state migration.

28.0 Chapter Contents

28.1 Thermal Migration through a Barrier

Consider the system represented schematically in the figure below.

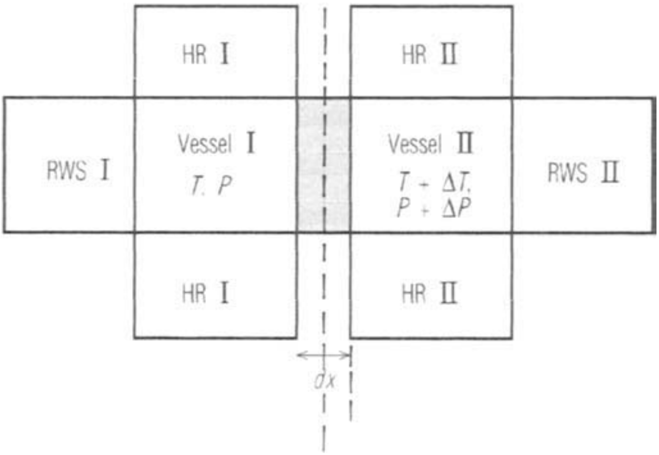

Fig. 28.1 Thermal migration through a barrier

Two vessels containing a single-component fluid are connected via a barrier that may be, e.g., a porous plate, a membrane, or a capillary. The two vessels are not at the same temperature or pressure. In each vessel, the temperature and pressure is maintained constant by coupling the vessel with its own heat reservoir, HR, and reversible work source, RWS. Thus, the temperature and pressure differences, ΔT and ΔP, are constant in any given case but may vary from case to case. To simplify matters, we consider flow through the barrier only in the x-direction.

The barrier is considered to be of infinitesimal thickness, dx. This allows us to dispense with an analysis of any processes that might occur inside the barrier itself. They may be deemed negligible without prejudicing the main conclusions we wish to draw from our thought experiment.

Two subsystems connected by an infinitesimal barrier represent a *discrete* composite system. By contrast, in Chapter 27 we considered *continuous* systems. In a discrete system we may replace the gradients of the intensive parameters by their differences. The fluxes and the driving forces will be the x-components, J_x and F_x, of the vectors, $\boldsymbol{J}$ and $\boldsymbol{F}$. The y- and z-components are deemed to vanish. We write the x-components simply as J and F, omitting the subscript for convenience. Thus, e.g., the x-component of the energy flux, J_U, will be written J_U, not J_{Ux}.

28.2 The Phenomenological Equations in the Entropy Production Representation

In the entropy production representation the fluxes are the energy flux, J_U, and the matter flux, J_N. These are driven by the conjugate discontinuous driving forces

$$F_U = \Delta\left(\frac{1}{T}\right) \qquad \text{and} \qquad F_N = \Delta\left(-\frac{\mu}{T}\right) \tag{28.2$_1$}$$

[cf. Eqs.(27.2)$_2$ and (27.2)$_3$]. The first is the *thermal*, the second the *diffusional*, driving force.

In analogy to Eq.(27.2)$_1$ the entropy production function becomes

$$\Phi = J_U F_U + J_N J_N\ , \tag{28.2$_2$}$$

i.e.,

$$\Phi = J_U \Delta(1/T) + J_N \Delta(-\mu/T)\ , \tag{28.2$_3$}$$

and, by Postulate VII, the phenomenological equations become

$$J_U = L_{UU} F_U + L_{UN} F_N \tag{28.2$_4$}$$

and

$$J_N = L_{NU} F_U + L_{NN} F_N\ . \tag{28.2$_5$}$$

Equation $(28.2)_4$ expresses the energy flux as the sum of the energy transported as heat and the energy transported by the diffusing particles of the fluid. Equation $(28.2)_5$ states that only particles with sufficient energy (in excess of the average energy of the bulk fluid), can pass the barrier. Energy depends on temperature. Hence, the matter flux depends on the thermal as well as the diffusional driving force.

The *cross coefficient* L_{NU} represents the tendency of the thermal driving force, $\Delta(1/T)$, to give rise to a flow of matter. Similarly, L_{UN} represents the tendency of the diffusional driving force, $\Delta(-\mu/T)$, to give rise to a flow of energy. By Postulate VIII, $L_{UN} = L_{NU}$. While the two cross coefficients are identical, their physical interpretations are different (cf. § 27.7).

28.3 The Phenomenological Equations in the Energy Retention Representation

In the energy retention representation the fluxes become the entropy flux, J_S, and the matter flux, J_N, and these will be driven by the conjugate discontinuous driving forces

$$Z_S = \Delta T \qquad \text{and} \qquad Z_N = \Delta\mu\,, \tag*{$(28.3)_1$}$$

[cf. Eqs.$(27.3)_2$ and $(27.3)_3$]. Z_S and Z_N are again the *thermal* and the *diffusional* driving forces.

In analogy to Eq.$(27.3)_1$ the energy retention function becomes

$$\Upsilon = J_S Z_S + J_N Z_N\,, \tag*{$(28.3)_2$}$$

i.e.,

$$\Upsilon = J_S \Delta T + J_N \Delta\mu\,. \tag*{$(28.3)_3$}$$

With the phenomenological coefficients, Λ_{KL}, the phenomenological equations now become

$$J_S = \Lambda_{SS} Z_S + \Lambda_{SN} Z_N \tag*{$(28.3)_4$}$$

and

$$J_N = \Lambda_{NS} Z_S + \Lambda_{NN} Z_N\,. \tag*{$(28.3)_5$}$$

Again, $\Lambda_{SN} = \Lambda_{NS}$ by Postulate VIII although the two cross coefficients have different physical interpretations (cf. § 27.7).

28.4 The Entropy of Transport

We now make use of the phenomenological equations in the *energy retention representation* to derive the first of the quantities of transport. Consider isothermal diffusion. Because $\Delta T = 0$, the thermal driving force, $Z_S = \Delta T$, vanishes and Eqs. $(28.3)_4$ and $(28.3)_5$ yield

$$J_S = \frac{A_{SN}}{A_{NN}}\, J_N = s^* J_N \,. \tag{28.4}$$

Since J_S is the entropy flow vector while J_N is the matter flow vector, s^* is the entropy transported per mole of matter at constant temperature and is therefore called the *entropy of transport.*

28.5 The Energy of Transport

The phenomenological equations in the *entropy production representation* furnish the second of the quantities of transport. Again we consider isothermal diffusion. Because we now have $\Delta(1/T) = 0$, the thermal driving force, $F_U = \Delta(1/T)$, again vanishes and Eqs. $(28.2)_4$ and $(28.2)_5$ yield

$$J_U = \frac{L_{UN}}{L_{NN}}\, J_N = u^* J_N \tag{28.5}$$

where u^* is the energy transported per mole of matter at constant temperature and is therefore called the *energy of transport.*

28.6 Interrelation between the Entropy and Energy of Transport

Consider the isothermal transport of a single matter species. By Eq.$(27.1)_3$ the energy flux is $J_U = J_Q + J_M$ where J_U is given by Eq.(28.5), and $J_M = \mu J_N$. The heat flux thus becomes

$$J_Q = (u^* - \mu) J_N \,. \tag{28.6$_1$}$$

But $J_Q = T J_S$ by Eqs. $(27.1)_1$. Thus, using Eq.(28.5) yields

$$J_Q = T s^* J_N \,. \tag{28.6$_2$}$$

Equating the two relations then furnishes

$$u^* = T s^* + \mu \,, \tag{28.6$_3$}$$

and this establishes the link between the energy and entropy of transport.

28.7 The Entropy of Transport by an Alternative Method

In § 28.4 we have derived the entropy of transport from the phenomenological equations in the energy retention representation. We now demonstrate the use of a transformation of vector fluxes and driving forces (cf. § 26.7) to derive it from the phenomenological equations in the entropy production representation. We write these as

$$J'_U = L_{UU}F'_U + L_{UN}F'_N \qquad (28.7)_1$$

and

$$J'_N = L_{UN}F'_U + L_{UN}F'_N \qquad (28.7)_2$$

[cf. Eqs.(27.5)$_1$ and (27.5)$_2$].

To derive the entropy of transport from these equations we transform them using Eqs.(26.7)$_1$ and (26.7)$_2$. The first task is the selection of the transformation variable, I. By Eq.(27.1)$_3$, $J_U = J_S + \mu N$ and this suggests the use of μ for I. Thus, we obtain

$$J'_U = J_U - \mu J_N \qquad \text{and} \qquad J'_N = J_N \qquad (28.7)_3$$

for the transformation of the fluxes, and

$$F'_U = F_U \qquad \text{and} \qquad F'_N = F_N + \mu F_U\ , \qquad (28.7)_4$$

for that of the forces. Substituting these equations into Eqs.(28.7)$_1$ and (28.7)$_2$ yields the transformed phenomenological equations in the entropy production representation as

$$J_U - \mu J_N = (L_{UU}+\mu L_{UN})F_U + L_{UN}F_N \qquad (28.7)_5$$

and

$$J_N = (L_{NU}+\mu L_{NN})F_U + L_{NN}F_N \qquad (28.7)_6$$

in terms of J_U and J_N. Now, in isothermal diffusion the thermal driving force, F_U, vanishes and we obtain

$$J_U = \left(\frac{L_{UN}}{L_{NN}} + \mu\right) J_N\,. \qquad (28.7)_7$$

But $J_U = u^*\, J_N$ by Eq.(28.5). Hence,

$$\frac{L_{UN}}{L_{NN}} = u^* - \mu\ , \qquad (28.7)_8$$

and, by the discrete composite system analog of Eq.(25.4)$_4$,

$$J_S = \frac{1}{T} J_U - \frac{\mu}{T} J_N \, . \tag{28.7)$_9$}$$

Using Eq.(28.5) again, we find

$$J_S = \frac{1}{T} J_U - \frac{\mu}{T} J_N = \frac{u^* - \mu}{T} \, J_N \, . \qquad (28.7)_{10}$$

But $u^* - \mu = Ts^*$ by Eq.(28.6)$_3$. Hence, we recover Eq.(28.4) for the entropy of transport.

28.8 Equivalence of the Entropy Production and Energy Retention Representations

We had first derived the expression for the entropy of transport, J_S, from the phenomenological equations in the energy retention representation, Eqs.(28.3)$_4$ and (28.3)$_5$. In the preceding section we derived J_S from the phenomenological equations in the entropy production representation, Eqs.(28.7)$_1$ and (28.7)$_2$. Thus, as it should, the same result is obtained, regardless of the representation selected. This served to demonstrate the equivalence of the representations by the pivotal equations of linear steady-state thermodynamics and parallels the equivalence of the representations by the cardinal equations of the equilibrium theory (cf. § 3.1).

28.9 The Heat of Transport

Let us now make another transformation based on the entropy production representation. Since we are seeking an expression for the transport quantity called the heat of transport, let the transformation variable I be h, the molar enthalpy of the fluid. The transformations become

$$J''_U = J_U - h\, J_N \qquad \text{and} \qquad J''_N = J_N \qquad (28.9)_1$$

and

$$F''_U = F_U \qquad \text{and} \qquad F''_N = F_N + h\, F_U \, . \qquad (28.9)_2$$

With these substitutions for the driving forces the phenomenological equations take the form

$$J''_U = (L_{UU} + h\, L_{UN})\, F_U + L_{UN}\, F_N \qquad (28.9)_3$$

and

$$J''_N = (L_{NU} + \, h\, L_{NN})\, F_U + L_{NN}\, F_N \, . \qquad (28.9)_4$$

When the temperature is constant, F_U again vanishes and we obtain

$$J''_U = \frac{L_{UN}}{L_{NN}} J''_N \,. \tag{28.9$_5$}$$

But $J''_U = J_U - hJ_N$ by the first of Eqs.(28.9)$_1$ and $J_U = u^* J_N$ by Eq.(28.5) so that

$$\frac{L_{UN}}{L_{NN}} = u^* - h \tag{28.9$_6$}$$

and

$$J''_U = (u^* - h)\, J''_N \,. \tag{28.9$_7$}$$

The quantity

$$q^* = u^* - h \tag{28.9$_8$}$$

is the *heat of transport*. We proceed to examine its meaning.

28.10 Meaning of the Heat of Transport

Consider an isothermal transfer of dN moles of fluid from Vessel I to Vessel II in Fig. 28.1. By definition, the energy flow is u^*dN and this would be energy lost from Vessel I if no other process took place. However, Vessel I is maintained at constant temperature, T, by the absorption of the heat $\delta Q^{\mathrm{HR\text{-}I}}$ from the heat reservoir I, and at constant pressure, P, by the performance of the work $\delta \mathrm{W}^{\mathrm{RWS\text{-}I}}$ on the system by the reversible work source I. Hence,

$$dU = -u^* dN + \delta Q^{\mathrm{HR\text{-}I}} + \delta \mathrm{W}^{\mathrm{RWS\text{-}I}} \tag{28.10$_1$}$$

is the change in the internal energy in Vessel I. But $dU = -u\,dN$ and $dV = -v\,dN$ since both decrease. Therefore, $\delta \mathrm{W}^{\mathrm{RWS\text{-}I}} = Pv\;dN$, and we have

$$\delta Q^{\mathrm{HR\text{-}I}} = (u^* - u - Pv)\,dN = (u^* - h)\,dN \,. \tag{28.10$_2$}$$

Consequently, $u^* - h = q^*$ is the heat per mole of matter leaving Vessel I, which is absorbed from the reservoir to maintain constant temperature. It is thus a pure heat flow but not between the two vessels. It is the heat flow from the reservoir to the vessel at the lower temperature, i.e., the vessel from which matter diffuses across the barrier. The heat of transport is thus the heat exchanged with the reservoir per mole of matter.

The quantity q^* is seen to be the amount of energy by which u^* exceeds the molar enthalpy of the fluid in the state characterized by the temperature, T, and the pressure, P. We note that, while u^* and h are defined only within an arbitrary constant, their difference, q^* is, at least in principle, a quantity amenable to direct calorimetric measurement.

Finally, we may rewrite Eq.(28.9)$_7$ in the form

$$J_{Q'} = q^* J_N \qquad (28.10)_3$$

to emphasize that we are dealing with a pure heat flow. J_Q is also a pure heat flow [cf. Eq.(27.8)$_1$] but the two differ in their nature. As we have seen, $J_Q = TJ_S$ is related to the entropy transported between the two vessels, while $J_{Q'}$ is related to the entropy transported from the heat reservoir to the vessel at the lower temperature.

29. USES OF THE HEAT OF TRANSPORT

The heat of transport is a true thermodynamic quantity capable of experimental determination. It is essential in the definition of the *thermomolecular pressure effect* and the *thermomechanical effect*. These are the subjects of the first four sections of this chapter. The last section reexamines the problem of the measurability of mass action in an open system that had been deferred from § 2.10.

29.0 Chapter Contents

29.1 The Thermomolecular Pressure Effect

The two vessels in Fig. 28.1 are maintained at their respective temperatures and pressures by the heat reservoirs and reversible work sources but they are not in contact with a matter reservoir. Hence, some time after the restrictions on the barrier have been removed (i.e., after it has been made diathermal and permeable), a dynamic equilibrium will be established with respect to matter exchange (diffusion). Thus, the matter flow will effectively cease. The system is then in a steady state which is maintained by the (constant) temperature difference, ΔT, between the two vessels. This temperature difference entails a concomitant pressure difference, ΔP. We seek the relation that links ΔP and ΔT at the temperature T.

To derive the relation, we will need to express the fluxes, J_U'' and J_N'', as functions of ΔT and ΔP. First, however, we rewrite the driving forces. Admitting that μ may depend on T, and substituting the identities [see Eqs. $(28.2)_1$]

$$F_U = \Delta(1/T) = -\Delta T/T^2 \qquad (29.1)_1$$

and

$$F_N = \Delta(-\mu/T) = -\Delta\mu/T + \mu\,\Delta T/T^2 \qquad (29.1)_2$$

into Eqs. $(28.9)_2$, we obtain

$$F_U = -\frac{1}{T^2}\,\Delta T \qquad (29.1)_3$$

for the thermal, and

$$F_N = -\frac{1}{T}\Delta\mu - (h-\mu)\frac{1}{T^2}\Delta T = -\frac{1}{T}\Delta\mu - \frac{s}{T}\Delta T\,, \tag{29.1)$_4$}$$

or, making use of the Gibbs-Duhem equation, Eq.(8.22)$_4$,

$$F_N = -v\,\Delta P/T\,, \qquad (29.1)_5$$

for the diffusional driving force. The phenomenological equations can therefore be written in the form

$$J_U = -\frac{L_{UU}}{T^2}\Delta T - \frac{v\,L_{UN}}{T}\Delta P \qquad (29.1)_6$$

and

$$J_N = -\frac{L_{NU}}{T^2}\Delta T - \frac{v\,L_{NN}}{T}\Delta P\,. \qquad (29.1)_7$$

When a steady state has been reached, the matter flow will have ceased. Since then $J_N = 0$, we find

$$\frac{\Delta P}{\Delta T} = -\frac{1}{Tv}\frac{L_{NU}}{L_{NN}}\,. \qquad (29.1)_8$$

Making use of the reciprocity relation, $L_{NU} = L_{UN}$, and using Eqs. (28.9)$_6$ and (28.9)$_8$, we obtain

$$\frac{L_{NU}}{L_{NN}} = \frac{L_{UN}}{L_{NN}} = u* - h = q*. \qquad (29.1)_9$$

Hence,

$$\Delta P = -\frac{q*}{vT}\Delta T\,. \qquad (29.1)_{10}$$

This steady-state equation describes the effect known as the *thermomolecular pressure effect.* It links changes in pressure and in temperature in the steady state when matter flow has ceased. It is not an equilibrium state since the heat flux does not vanish. The effect is determined by the heat of transport, $q*$.

29.2 The Thermomechanical Effect

Suppose now that we keep the temperature constant throughout the system, so that $\Delta T = 0$, but maintain a pressure difference, ΔP. This will result in a flow of matter from one vessel to the other, accompanied by a flow of energy which can be measured by measuring the amount of heat required to keep the temperature constant. The two flows are proportional and the proportionality constant is again the heat of transport, q^*.

We can deduce this from the phenomenological equations, Eq.$(29.1)_6$ and $(29.1)_7$. When $\Delta T = 0$, we have

$$\frac{J_U}{J_N} = \frac{L_{UN}}{L_{NN}} \qquad (29.2)_1$$

or, using Eq.$(29.1)_9$,

$$J_U = q^* J_N \,. \qquad (29.2)_2$$

This effect is known as the *thermomechanical effect*. It relates the matter flux to the energy flux at constant temperature via the heat of transport, q^*.

29.3 Interrelation between the Thermomechanical and the Thermomolecular Pressure Effect

The reciprocity relation $L_{UN} = L_{NU}$ establishes the link between the thermomechanical effect and the thermomolecular pressure effect. Combining Eqs.$(29.1)_8$ and $(29.2)_1$, we find

$$\left.\frac{\Delta P}{\Delta T}\right|_{J_N=0} = -\left.\frac{1}{vT}\frac{J_U}{J_N}\right|_{\Delta T=0} . \qquad (29.3)$$

Because of the relation between them, both effects will always be manifest in the same system.

29.4 Thermodynamic Steady-State Equations

In the steady state Eq.$(29.1)_{10}$ is an example of a true thermodynamic equation in that it is a necessary relation between thermal and mechanical quantities that can all be measured. The reciprocity relations (Postulate VIII) are valid whether a steady state has been reached or not as long as the relations between fluxes and driving forces are linear. However, in the non-steady-state the phenomenological coefficients are kinetic coefficients and must be determined by actual measurements of the rates or from a molecular model. In steady-state thermal migration, by contrast, q^* can be measured directly, at least in principle, by calorimetric measurements.

29.5 Measurability of Mass Action in an Open System

In § 2.10 we deferred discussion of the measurability of mass action in an open system to this section. We are now ready to take it up again and concern ourselves with the mass action representing the change in internal energy resulting from the occurrence of a pure matter flow at constant temperature and pressure. Consider an isolated system composed of two subsystems which are initially divided by a diathermal and movable but impermeable barrier. The system is in contact with a heat reservoir and a reversible work source, and is thus kept at constant temperature and pressure. If now the barrier is made permeable to the species of interest, then the energy transported per mole of matter at constant temperature and pressure in the steady state from the subsystem having the higher chemical potential to that having the lower potential (cf. § 4.10), is

$$u^* = q^* + h \tag*{(29.5)$_1$}$$

by Eq.(28.9)$_8$. Here q^*, the heat of transport, is the heat exchanged with the reservoir per mole of matter, and h is the molar enthalpy of the diffusing species. The energy of transport, u^*, is free from the heat (entropy) carried by the diffusing matter. Although q^* can be measured, the molar enthalpy of the fluid is defined—as are all thermodynamic potentials—with respect to a reference that depends on the circumstances under which h is determined. It may be obtained from *Kirchhoff's* equation [cf. Eq.(21.8)$_1$]

$$h = h_o + \int_{T_o}^{T} c_P(T')\,dT' \tag*{(29.5)$_2$}$$

where h_o is the molar enthalpy at the reference temperature T_o and the (constant) pressure P. Thus u^* is obtained within the same constraints. Keeping this in mind, we obtain the change in internal energy caused by the mass action as

$$\Delta U = N(u^* - u_o^*) = Nq^* + \Delta H \tag*{(29.5)$_3$}$$

where N is the total number of moles transported, u_o^* is the reference energy of transport and $\Delta H = N(h - h_o)$. Since $W = 0$, and $Q = 0$ also (no heat, except Nq^*, flowing in or out of the system), we then have

$$M = N(u^* - u_o^*)\,. \tag*{(29.5)$_4$}$$

as the mass action due to the diffusional flow. Thus, unless u_o^* can be obtained independently, the mass action M can be determined only within the uncertainty of not knowing the reference energy of transport.

30. MINIMUM ENTROPY PRODUCTION

To conclude Part II we show that the linear steady state is a *state of minimum entropy production*. This represents the most general result of the theory of steady-state thermodynamics.

30.0 Chapter Contents

30.1 The Rate of Entropy Production in the General Case

Let us consider a thermodynamic system, initially not in a steady state, in which the thermodynamic forces and fluxes vary with time within the system but remain constant at its boundaries so that the system can eventually reach a steady state. In such a system the rate of entropy production, and therefore also the entropy production function, change with time. Thus we may write

$$\Theta(t) = \int_V \Phi(t)\, dv = \int_V \sum\nolimits_k \boldsymbol{J}_k(t) \cdot \boldsymbol{F}_k(t)\, dv \qquad (30.1)_1$$

where V is the volume.

Let us now consider $d\Theta(t)/dt$, the time rate of change of the rate of entropy production. Differentiation of $\Theta(t)$ with respect to time yields

$$\frac{d\Theta(t)}{dt} = \frac{d_F\Theta(t)}{dt} + \frac{d_J\Theta(t)}{dt} \qquad (30.1)_2$$

where

$$\frac{d_F\Theta(t)}{dt} = \int_V \sum\nolimits_k \boldsymbol{J}_k(t) \cdot \frac{\partial \boldsymbol{F}_k(t)}{\partial t}\, dv < 0 \qquad (30.1)_3$$

is that part of the rate at which $\Theta(t)$ changes with time because the driving forces change, while

$$\frac{d_J\Theta(t)}{dt} = \int_V \sum\nolimits_k \frac{\partial \boldsymbol{J}_k(t)}{\partial t} \cdot \boldsymbol{F}_k(t)\, dv \qquad (30.1)_4$$

is that part which arises from changes of the fluxes with time.

In the general case we can say nothing[23] about the sign of $d\Theta(t)/dt$. The first term in Eq.$(30.1)_2$ is bound to be negative if the conditions at the boundaries of the system are constant (see Appendix 7). Nothing, however, can be inferred about the second term because it can carry any sign in the general, non-equilibrium, case.

30.2 The Rate of Entropy Production in the Steady State

Consider therefore now what happens when the system that we have just discussed approaches a linear steady state. By Postulate VII the fluxes depend linearly on the driving forces, i.e.,

$$J_k = \sum\nolimits_l L_{kl} \boldsymbol{F}_l \,, \tag{30.2)$_1$}$$

and by Postulate VIII, the phenomenological coefficients obey the reciprocity relations, i.e., $L_{kl} = L_{lk}$. Furthermore, all these quantities are independent of time by Postulate VI.

Taking the limit as t becomes constant, and inserting Eq.$(30.2)_1$ into Eqs.$(30.1)_3$ and $(30.2)_4$ yields

$$\lim_{t \to const} \frac{d_F\Theta(t)}{dt} = \frac{d_F\Theta}{dt} = \int_V \sum\nolimits_{kl} L_{kl} \boldsymbol{F}_k \cdot \frac{\partial \boldsymbol{F}_k}{\partial t}\, dv \qquad (30.2)_2$$

and

$$\lim_{t \to const} \frac{d_J\Theta(t)}{dt} = \frac{d_J\Theta}{dt} = \int_V \sum\nolimits_{kl} L_{kl} \frac{\partial \boldsymbol{F}_k}{\partial t} \cdot \boldsymbol{F}_k\, dv \,. \qquad (30.2)_3$$

But the two integrals are identical because—as just asserted—they are invariant with respect to an interchange of the indices k and l because the reciprocity relations hold. Hence,

$$\frac{d_F\Theta}{dt} = \frac{d_J\Theta}{dt} \,, \qquad (30.2)_4$$

i.e., as the steady state is approached the contribution to the rate of entropy production due to the time changes of the fluxes and the contribution due to the driving forces approach equality.

30.3 The State of Minimum Entropy Production

It follows from the foregoing that in the steady state the time rate of change of the rate of entropy production becomes

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[23] See, e.g., Wisniewski et al. (1976), p.44.

$$\frac{d\Theta}{dt} = 2\frac{d_F\Theta}{dt} = 2\frac{d_J\Theta}{dt}\,. \qquad (30.3)_1$$

It is then still true that $d_F\Theta/dt$ is a negative quantity if the conditions at the boundaries of the system are stationary so that the system can attain a steady state (see Appendix 7).. However, now $d_J\Theta/dt$ is also negative because it is equal to $d_F\Theta/dt$. Thus

$$\frac{d\Theta}{dt} \leq 0\,, \qquad (30.3)_2$$

i.e., the time rate of change of the entropy production decreases as the system approaches the (linear) steady state, until a minimum is reached in that state. The equality holds whenever the steady state has been attained. The linear steady state is thus a state of minimum entropy production.

A1. EXACT AND INEXACT DIFFERENTIALS

This chapter presents a brief discussion of exact and inexact differentials.

A1.0 Contents

A1.1 The Equation of Integrability

Consider a thermodynamic function, $U = U(S, V)$, where U and S are functions of state. The total differential, dU, is then an exact differential. To show this, we set

$$dU = X(S, V)\,dS + Y(S, V)\,dV \tag*{(A1.1)$_1$}$$

where

$$X(S, V) = \left.\frac{\partial U}{\partial S}\right|_V \quad \text{and} \quad Y(S, V) = \left.\frac{\partial U}{\partial V}\right|_S . \tag*{(A1.1)$_2$}$$

Now, if dU is an exact differential as asserted, mixed derivatives do not depend on the order of differentiation. Thus

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}, \tag*{(A1.1)$_3$}$$

and it further follows that

$$\left.\frac{\partial X(S, V)}{\partial V}\right|_S = \left.\frac{\partial Y(S, V)}{\partial S}\right|_V . \tag*{(A1.1)$_4$}$$

The last equation is the *equation of integrability*. It must be satisfied, as it is here, for the differential dU to be an exact differential. It thus constitutes a test for the exactness of a differential.

A1.2 The Exact Differential

Let us test the relation

$$dU = T dS - P dV \tag*{(A1.2)$_1$}$$

for exactness. We now have $X(S,V) = T$, and $Y(S,V) = -P$, and thus Eq.(A1.1)$_4$ becomes

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V. \tag{A1.2$_2$}$$

But this is the first of the Maxwell relations, Eq.(10.6)$_1$, asserting that mixed derivatives do not depend on the order of differentiation. Thus the equation of integrability is satisfied.

A1.3 The Inexact Differential

Now consider the differential $dU = dQ + dW$ where $dW = -PdV$ and neither Q nor W are functions of state. We wish to ascertain if

$$\mathrm{d}Q = \mathrm{d}U + P\mathrm{d}V \tag{A1.3$_1$}$$

is an *exact* differential. To subject it to the test of Eq.(A1.4), we first express dU in the form

$$dU = \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV \tag{A1.3$_2$}$$

and then substitute this into $dQ = dU + PdV$. The substitution yields

$$dQ = \left.\frac{\partial U}{\partial S}\right|_V dS + \left[\left.\frac{\partial U}{\partial V}\right|_S + P\right] dV \tag{A1.3$_3$}$$

and comparison with Eq.(A1.1)$_1$ shows that

$$X(S,V) = \left.\frac{\partial U}{\partial S}\right|_V \tag{A1.3$_4$}$$

while

$$Y(S,V) = \left.\frac{\partial U}{\partial V}\right|_S + P. \tag{A1.3$_5$}$$

Thus

$$\left.\frac{\partial X}{\partial V}\right|_S = \frac{\partial^2 U}{\partial V \partial S} \tag{A1.3$_6$}$$

and

$$\left.\frac{\partial Y}{\partial S}\right|_V = \frac{\partial^2 U}{\partial S \partial V} + \left.\frac{\partial P}{\partial S}\right|_V . \qquad \text{(A1.3)}_7$$

Clearly, the equation of integrability is not satisfied and dQ is therefore an *inexact* differential. To emphasize this distinction inexact differentials are written in this text as δQ, δW, δM, etc., instead of dQ, dW, and dM, etc.

A2. JACOBIANS

Jacobians are determinants whose elements are partial derivatives. They are widely used in thermodynamics largely because of their usefulness in manipulating derivatives. The key to their use is the relation

$$\left.\frac{\partial u}{\partial x}\right|_{y,\ldots z} = \frac{\partial(u, y, \ldots z)}{\partial(x, y, \ldots z)} \tag{A2.0}$$

which expresses a partial derivative as a Jacobian. The quantities which are kept constant in the derivative are incorporated in the Jacobian. The following sections discuss some of their properties and applications.

A2.0 Contents

A2.1 Definition

Let $u, v, \ldots w$ be functions of $x, y, \ldots z$. Then the Jacobian is defined as

$$\frac{\partial(u, v, \ldots w)}{\partial(x, y, \ldots z)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \cdots & \frac{\partial u}{\partial z} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} & \cdots & \frac{\partial v}{\partial z} \\ \vdots & \vdots & & \vdots \\ \frac{\partial w}{\partial x} & \frac{\partial w}{\partial y} & \cdots & \frac{\partial w}{\partial z} \end{vmatrix} . \tag{A2.1}$$

Inside the determinant we have omitted, for simplicity, to indicate the variables being held constant.

A2.2 Properties

The five properties of Jacobians that are most useful in thermodynamics are listed below without proof. Thorough discussions can be found in any good text on calculus.

__1. Reciprocals:__

$$\frac{\partial(u, v, \ldots w)}{\partial(x, y, \ldots z)} = 1 \Big/ \frac{\partial(x, y, \ldots z)}{\partial(u, v, \ldots w)} \tag{A2.2$_1$}$$

2. Row or column interchange:

$$\frac{\partial(u,v,\dots w)}{\partial(x,y,\dots z)} = -\frac{\partial(v,u,\dots w)}{\partial(x,y,\dots z)} \qquad (A2.2)_2$$

3. Chain rule:

$$\frac{\partial(u,v,\dots w)}{\partial(x,y,\dots z)} = \frac{\partial(u,v,\dots w)}{\partial(\mathrm{r},\mathrm{s},\dots \mathrm{t})}\frac{\partial(\mathrm{r},\mathrm{s},\dots \mathrm{t})}{\partial(x,y,\dots z)} \qquad (A2.2)_3$$

4. Determinant expansion:

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \left.\frac{\partial u}{\partial x}\right|_y & \left.\frac{\partial u}{\partial y}\right|_x \\ \left.\frac{\partial v}{\partial x}\right|_y & \left.\frac{\partial v}{\partial y}\right|_x \end{vmatrix} = \left.\frac{\partial u}{\partial x}\right|_y \left.\frac{\partial v}{\partial y}\right|_x - \left.\frac{\partial u}{\partial y}\right|_x \left.\frac{\partial v}{\partial x}\right|_y \qquad (A2.2)_4$$

or

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,y)}{\partial(x,y)}\frac{\partial(v,x)}{\partial(y,x)} - \frac{\partial(u,x)}{\partial(y,x)}\frac{\partial(v,y)}{\partial(x,y)}\,. \qquad (A2.2)_5$$

5. Maxwell relations:

Let x_1, y_1 and x_2, y_2 be pairs of conjugate extensive (x) and intensive (y) parameters. Then the four possible Maxwell relations are

$$\left.\frac{\partial x_1}{\partial y_2}\right|_{y_1} = \mathrm{sgn}(y_2x_2)\left.\frac{\partial x_2}{\partial y_1}\right|_{y_2}, \qquad \left.\frac{\partial y_1}{\partial x_2}\right|_{x_1} = \mathrm{sgn}(y_2x_2)\left.\frac{\partial y_2}{\partial x_1}\right|_{x_2}, \qquad (A2.2)_6$$

$$\left.\frac{\partial x_1}{\partial x_2}\right|_{y_1} = -\,\mathrm{sgn}(y_2x_2)\left.\frac{\partial y_2}{\partial y_1}\right|_{x_2}, \quad \text{and} \quad \left.\frac{\partial y_1}{\partial y_2}\right|_{x_1} = -\,\mathrm{sgn}(y_2x_2)\left.\frac{\partial x_2}{\partial x_1}\right|_{y_2}, \qquad (A2.2)_7$$

where $\mathrm{sgn}(y_2x_2)$ takes the values $+1$ or -1, according to the sign of the y_2x_2–term in the Euler equation, Eq.$(3.10)_2$. A demonstration of the use of these equations follows.

A2.3 Applications

Below we illustrate the use of Jacobians in thermodynamics on hand of several typical applications.

1. Find the corresponding member in a Maxwell relation (cf. § 10.7)

We wish to find the corresponding member when $(\partial\mu/\partial S)_N$ is given. Since μ is an intensive, and S is an extensive parameter, the appropriate relation to use is Eq.(A2.2)$_{6.2}$. Inserting the values $y_1 = \mu$, $x_1 = N$, $x_2 = S$, $y_2 = T$, and $\mathrm{sgn}(y_2 x_2) = \mathrm{sgn}(TS) = 1$, immediately yields

$$\left.\frac{\partial\mu}{\partial S}\right|_N = \left.\frac{\partial T}{\partial N}\right|_S \qquad (\text{A2.3})_1$$

[cf. the second of Eqs.(10.6)$_1$ and the second of Eqs.(10.6)$_3$, the first at constant volume, and the second at constant pressure, respectively.].

2. Show that $C_P/C_V = \kappa_T/\kappa_S$ (cf. § 10.3) (A2.3)$_2$

Written out explicitly the relation becomes

$$\left.\frac{\partial S}{\partial T}\right|_P \left.\frac{\partial T}{\partial S}\right|_V = \left.\frac{\partial V}{\partial P}\right|_T \left.\frac{\partial P}{\partial V}\right|_S . \qquad (\text{A2.3})_3$$

Recast in terms of Jacobians, we have

$$\frac{\partial(S,P)}{\partial(T,P)}\frac{\partial(T,V)}{\partial(S,V)} = \frac{\partial(V,T)}{\partial(P,T)}\frac{\partial(P,S)}{\partial(V,S)} \qquad (\text{A2.3})_4$$

and this is clearly an identity since it involves an even number of interchanges.

3. Show that $\alpha_P/\alpha_S = 1 - C_P/C_V$ (cf. § 10.3) (A2.3)$_5$

This is not a simple identity and requires a little ingenuity. We write

$$\frac{\alpha_S}{\alpha_P} = \left.\frac{\partial V}{\partial T}\right|_S \left.\frac{\partial T}{\partial V}\right|_P = \frac{\partial(V,S)}{\partial(T,S)}\frac{\partial(T,P)}{\partial(V,P)} = -\frac{\partial(S,V)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(T,S)}\frac{\partial(T,P)}{\partial(V,P)} \qquad (\text{A2.3})_6$$

where, in the last term, we have both divided and multiplied by $\partial(T,P)$. We now expand the first of the last three Jacobians. This gives

$$\frac{\partial(S,V)}{\partial(T,P)} = \frac{\partial(S,P)}{\partial(T,P)}\frac{\partial(V,T)}{\partial(P,T)} - \frac{\partial(S,T)}{\partial(P,T)}\frac{\partial(V,P)}{\partial(T,P)} \qquad (\text{A2.3})_7$$

and therefore

$$\frac{\alpha_S}{\alpha_P} = -\left[\frac{\partial(S,P)}{\partial(T,P)}\frac{\partial(V,T)}{\partial(P,T)} - \frac{\partial(S,T)}{\partial(P,T)}\frac{\partial(V,P)}{\partial(T,P)}\right]\frac{\partial(T,P)}{\partial(T,S)}\frac{\partial(T,P)}{\partial(V,P)}\,. \qquad (\text{A2.3})_8$$

Carrying out the indicated multiplication and canceling terms where possible, yields

$$\frac{\alpha_S}{\alpha_P} = \frac{\partial(S,P)}{\partial(T,P)}\frac{\partial(V,T)}{\partial(T,S)}\frac{\partial(T,P)}{\partial(V,P)} + 1 = \frac{C_P}{T}\frac{\partial(V,T)}{\partial(T,S)}\frac{1}{V\alpha_P} + 1\,. \qquad (\text{A2.3})_9$$

Now we both divide and multiply the middle term on the right-hand-side by $\partial(V, S)$. This leads to

$$\frac{\alpha_S}{\alpha_P} = \frac{C_P}{T}\frac{\partial(V,T)}{\partial(V,S)}\frac{\partial(V,S)}{\partial(T,S)}\frac{1}{V\alpha_P} + 1 = \frac{C_P}{T}\left.\frac{\partial \mathrm{T}}{\partial \mathrm{S}}\right|_V \left.\frac{\partial V}{\partial T}\right|_S \frac{1}{V\alpha_P} + 1. \qquad (\text{A2.3})_{10}$$

Thus,

$$\alpha_S/\alpha_P = (C_P/C_V)(\alpha_S/\alpha_P) + 1 \qquad (\text{A2.3})_{11}$$

which then rearranges to the proposed identity.

4. Derive the difference between the heat capacities (cf. § 10.3)

We express C_V as a Jacobian and then manipulate it into the required form. We have

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V = T\frac{\partial(S,V)}{\partial(T,V)} = T\frac{\partial(S,V)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(T,V)} = -\frac{T}{V\kappa_T}\frac{\partial(S,V)}{\partial(T,P)} \qquad (\text{A2.3})_{12}$$

Expanding the Jacobian on the right as a determinant yields

$$C_V = -\frac{T}{V\kappa_T}\left[\left.\frac{\partial S}{\partial T}\right|_P \left.\frac{\partial V}{\partial P}\right|_T - \left.\frac{\partial S}{\partial P}\right|_T \left.\frac{\partial V}{\partial T}\right|_P\right]. \qquad (\text{A2.3})_{13}$$

Using the first of Eqs.$(10.6)_1$, i.e., the Maxwell relation

$$\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P = -V\alpha_P\,, \tag{A2.3$_{14}$}$$

and rewriting the other partial derivatives in terms of the members of the primary set gives at once

$$C_V = C_P - TV\alpha_P^2/\kappa_T\,. \tag{A2.3$_{15}$}$$

5. Express the Joule-Thompson coefficient, $(\partial T/\partial P)_H$, in terms of the members of the primary set.

This is a case where an *extensive* variable is held constant. We have

$$\left.\frac{\partial T}{\partial P}\right|_H = \frac{\partial(T,H)}{\partial(P,H)}\frac{\partial(T,P)}{\partial(T,P)} = -\frac{\partial(H,T)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(P,H)} = -\frac{1}{C_P}\left.\frac{\partial H}{\partial P}\right|_T\,. \tag{A2.3$_{16}$}$$

because $(\partial H/\partial T)_P = C_P$ [cf. Eq.(10.2)$_4$]. But $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$ at constant N. Hence,

$$\left.\frac{\partial H}{\partial P}\right|_T = T\left.\frac{\partial S}{\partial P}\right|_T + V = -T\left.\frac{\partial V}{\partial T}\right|_P + V, \tag{A2.3$_{17}$}$$

and we finally obtain

$$\left.\frac{\partial T}{\partial P}\right|_H = \frac{V}{C_P}\left(T\alpha_P - 1\right). \tag{A2.3$_{18}$}$$

A3. THE LEGENDRE TRANSFORMATION

Replacing an extensive variable in the fundamental equation with its intensive conjugate turns the fundamental equation into an equation of state with an attendant loss of information. The loss occurs because the intensive conjugate is a (partial) derivative. The Legendre transformation is a mathematical technique for interchanging dependent and independent variables in a functional relationship *without* incurring any loss of information. The transformation is therefore an indispensable tool of equilibrium thermodynamics (cf. §§ 8.5 and 8.6).

This Appendix treats the mathematics of the transformation. Thermodynamic applications. are used as illustrations where appropriate. We shall first introduce the concept of the Legendre transformation effecting a single interchange only. Such a single interchange is called a *first-order* Legendre transformation. *Higher-order* transformations, in which two or more conjugate parameters are interchanged, then follow.

A3.0 Contents

A3.1 First-order Legendre Transformations

The infinitesimal variation of a function

$$y^{(0)} = y^{(0)}(x_1, x_2, \ldots, x_n) \tag*{(A3.1)$_1$}$$

of the independent variables $x_1, \ldots, x_n$ is

$$dy^{(0)} = \xi_1 dx_1 + \xi_2 dx_2 + \ldots + \xi_n dx_n \tag*{(A3.1)$_2$}$$

where

$$\xi_i = \left.\frac{\partial y^{(0)}}{\partial x_i}\right|_{x(\neq x_i)} . \tag*{(A3.1)$_3$}$$

Consider now the function

$$y^{(1)} = y^{(0)} - \xi_1 x_1 \,. \qquad (A3.1)_4$$

Its variation is

$$dy^{(1)} = dy^{(0)} - d\xi_1 x_1 = dy^{(0)} - \xi_1 dx_1 \; - x_1 d\xi_1 \,, \qquad (A3.1)_5$$

and using Eq.$(A3.1)_2$, this becomes

$$dy^{(1)} = \; - x_1 d\xi_1 + \xi_2 dx_2 + \;\dots\; + \xi_n dx_n \,. \qquad (A3.1)_6$$

Now compare Eqs.$(A3.1)_2$ and $(A3.1)_6$. Clearly, the roles of x_i and ξ_i as independent and dependent variables has been interchanged. To effect this interchange it is merely necessary to subtract the product of x_1 with its conjugate partial derivative, ξ_1, from the base function, $y^{(0)}$. The resulting function,

$$y^{(1)} = y^{(1)}\,(\xi_1, x_2, \dots\, x_n) = y^{(0)}[\xi_1] \qquad (A3.1)_7$$

is called the first-order Legendre transform of the base function $y^{(0)}$ introducing the derivative ξ_1. The second equation introduces the bracket notation as a succinct shortcut. The choice of the first extensive independent variable, x_1, to be exchanged against ξ_1, is arbitrary (cf. § 18.8). The superscript in Eq.$(A3.1)_1$ is zero because the base function may formally be regarded as the Legendre transform of order zero.

A3.2 Information Content of the Transformation

It is perhaps not obvious from the foregoing that the exchange of x_1 against the partial derivative, ξ_1, has left the information content of $y^{(1)}$ the same as that of $y^{(0)}$. To see this more clearly, we turn to the geometrical interpretation of the transformation. For simplicity, we consider a functional relation in a single variable, $y = y(x)$. This relation represents a locus of points (a curve) in the x,y−plane. The curve is said to be defined by *point coordinates*. As illustrated by Fig. A3.2, a curve in two-dimensional space can, however, be represented equally well by the envelope formed by lines tangent to the curve at each point.

Let the tangent lines have slopes, ξ, and intercepts, ψ. The equation of the envelope, i.e., the equation of the curve, is $\psi = \psi(\xi)$, and the curve is said to be defined by *line coordinates*[24]. In three-dimensional space a curve would be defined by *surface coordinates*, i.e., by tangent surfaces. Extension to higher dimensions cannot be visualized but is straightforward mathematically.

The two functions, $y = y(x)$, and $\psi = \psi(\xi)$, clearly describe the same curve and thus contain the same information. In the notation of § A3.1, y is $y^{(0)}$, the base function, and ψ is $y^{(1)}$, the first-order Legendre transform of $y^{(0)}$. Despite the introduction of the

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[24] The geometry of line, surface, and higher coordinates was developed by J. Plücker (1868-69) and is sometimes referred to as Plücker geometry.

derivative, the transform preserves the information contained in the base function because it contains not only the slopes (i.e, the derivatives) but the intercepts as well. It therefore conytains the complete information on the envelope.

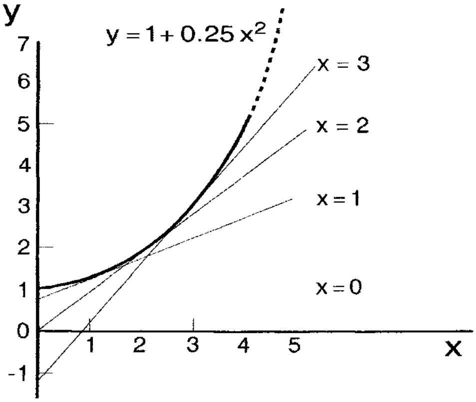

Fig. A3.2 Family of tangents to the curve $y = 1+0.25x^2$

Consider an example from the text. Let the base function be the internal energy, so that $y^{(0)} = U(S, V, N)$. An exchange of the entropy, S, against the temperature, T, i.e., letting $\xi = T$, yields the first-order Legendre transform $y^{(1)} = U[T]$, i.e., $F = U[T]$, in the form $F = F(T, V, N)$ where F is the free energy (cf. § 8.10).

A3.3 Duality of Point and Line Coordinates

Point and line coordinates are said to be *duals* of one another. The Legendre transformation exploits the duality between the two. The relation between the point coordinates, x, y, and the line coordinates, ψ, ξ, is easily derived with the aid of Fig. A3.3 below.

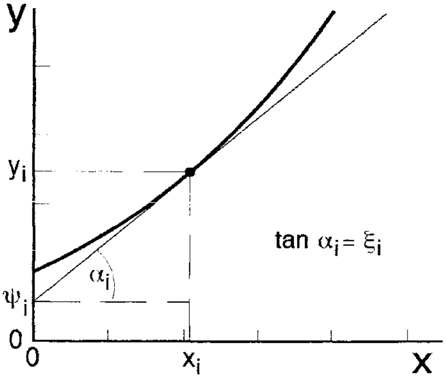

Fig. A3.3 The tangent, $L(\psi_i, \xi_i)$, at the point, $P(x_i, y_i)$

Consider a curve in two-dimensional space as shown above. Note the point, $P(x_i, y_i)$, along the curve, and its dual, the line, $L(\psi_i, \xi_i)$, that is tangent to the curve at that point. Clearly,

$$\tan \alpha_i = \frac{y_i - \psi_i}{x_i - 0}\,, \tag{A3.3$_1$}$$

and, therefore,

$$\xi_i = \tan \alpha_i = \left.\frac{dy}{dx}\right|_{x=x_i,\, y=y_i} \tag{A3.3$_2$}$$

and

$$\psi_i = y_i\,. \tag{A3.3$_3$}$$

For all points along the curve, then, the sought-for relation between the point and line coordinates is

$$\psi = y - \xi x \tag{A3.3$_4$}$$

given the functional relation $y = y(x)$. This equation should be compared with Eq.(A3.1)$_4$.

A3.4 Higher-order Legendre Transformations

The function

$$y^{(k)} = y^{(k)}(\xi_1, \ldots \xi_k, x_{k+1}, \ldots x_n) = y^{(0)}[\xi_1, \ldots \xi_k] \tag{A3.4$_1$}$$

where the $\xi_1, \ldots \xi_k$ are given by Eq.(A3.1)$_3$, is called the Legendre transform of order k of the base function $y^{(0)}$. The Legendre transformation that introduces the derivatives $\xi_1, \ldots \xi_k$ into the base function $y^{(0)}$ is

$$y^{(k)} = y^{(0)} - \sum_{i=1}^{i=k} \xi_i x_i\,. \tag{A3.4$_2$}$$

Let us illustrate this again with an example from the text. Exchanging both the entropy, S, and the volume, V, in the base function $y^{(0)} = U(S, V, N)$, furnishes the second-order Legendre transform, $y^{(2)} = U[T, P]$, or $G = G(T, P, N)$, where G is the free enthalpy (cf. § 8.16).

The differential form of Eq.(A3.4)$_2$ is

$$dy^{(k)} = dy^{(0)} - \sum_{i=1}^{i=k} d(\xi_i x_i)\,, \tag{A3.4$_3$}$$

or, since we have

$$dy^{(0)} = \sum_{i=1}^{i=n} \xi_i dx_i\,, \tag{A3.4$_4$}$$

[cf. Eq.(A3.1)$_2$], we may write

$$dy^{(k)} = -\sum_{i=1}^{i=k} x_i d\xi_i + \sum_{i=k+1}^{i=n} \xi_i dx_i \tag{A3.4$_5$}$$

as an alternative expression.

A3.5 The Complete Legendre Transform

The complete Legendre transform, the transform of order n, vanishes identically. This follows directly from the definition of the transform of order k, Eq.(A3.4)$_2$, since

$$y^{(n)} = y^{(0)} - \sum_{i=1}^{i=n} \xi_i x_i = 0\,. \tag{A3.5$_1$}$$

This is easily verified by looking at the Euler equation (cf § 3.10)

$$y^{(0)} - \sum_{i=1}^{i=n} \xi_i x_i = U - \sum_{i=1}^{i=n} Y_i X_i = 0\,. \tag{A3.5$_2$}$$

In thermodynamic theory this property of the complete Legendre transform gives rise to the Gibbs-Duhem equation (cf. § 8.22).

A3.6 The Inverse Legendre Transform

The inverse Legendre transform also follows from Eq.(A3.4)$_2$. It is

$$y^{(0)} = y^{(k)} + \sum_{i=1}^{i=k} \xi_i x_i\,. \tag{A3.6}$$

Letting k = 1, this correctly gives $U = F + TS$.

A3.7 Number of Partial Legendre Transformations

The number of transforms of order $0 < k < n$ is given by the combination

$$C(n, k) = \frac{n!}{(n-k)!\,k!}\,, \tag{A3.7$_1$}$$

where n is the number of variables of the base function, $y^{(0)}$, and k is the number of conjugate pairs involved in the transformation, $y^{(k)}$. Thus the total number of *partial* $(k = 1, \ldots, n-1)$ Legendre transforms is[25]

$$\sum_{k=1}^{k=n-1} C(n, k) = 2^n - 2 \tag{A3.7$_2$}$$

As the *total* number of Legendre transforms includes the complete transform, it is thus $2^n - 1$, that is, 1 more than the number of partial transforms.

A3.8 First-order Partial Derivatives of a Legendre Transform

There exist two useful relations involving the first-order partial derivatives of Legendre transforms. They will be stated here without derivation[26].

$$x_i = -\left.\frac{\partial y^{(k)}}{\partial \xi_i}\right|_{\xi(\neq\xi_i),\ldots x\ldots} \tag{A3.8$_1$}$$

and

$$\left.\frac{\partial y^{(k)}}{\partial x_j}\right|_{\xi_i,\ldots x(\neq x_j)\ldots} = \left.\frac{\partial y^{(0)}}{\partial x_j}\right|_{x_i,\ldots x(\neq x_j)\ldots} \tag{A3.8$_2$}$$

Employing the subscript notation for partial derivatives, these relations become

$$x_i = -y_i^{(k)} \tag{A3.8$_3$}$$

and

$$\left. y_j^{(k)}\right|_{\xi} = \left. y_j^{(0)}\right|_{x}\,. \tag{A3.8$_4$}$$

By the first of these relations the partial derivative of a Legendre transform with respect to the transform variable ξ_i is the negative of the conjugate variable of the latter, x_i. To apply them, let $y^{(0)} = U(S, V, N)$ so that $x_1 = S$, and further let $y^{(1)} = F(T, V, N)$. We then correctly find

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[25] see, e.g., Crystal (1961), p. 191.

[26] See Modell and Reid (1983), pp. 109-114.

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} . \qquad (A3.8)_5$$

By the second relations, the partial derivative of a Legendre transform with respect to any untransformed variable x_j is equal in value to the partial derivative of the base function with respect to the same variable, x_j. As an example, using the same functions as before, we have simply

$$\left.\frac{\partial F}{\partial V}\right|_{T,N} = \left.\frac{\partial U}{\partial V}\right|_{S,N} = -P \qquad (A3.8)_6$$

Equations $(A3.8)_2$ and $(A3.8)_4$ are almost trivial in application.

A3.9 Second-order Partial Derivatives of a Legendre Transform

Relations involving the second-order partial derivatives of $y^{(1)}$ and $y^{(0)}$ can also be established[20]. These relations are

$$y^{(1)}_{11} = -1/y^{(0)}_{11} \qquad (A3.9)_1$$

$$y^{(1)}_{1i} = y^{(0)}_{1i}/y^{(0)}_{11} \qquad (i \neq 1) \qquad (A3.9)_2$$

and

$$y^{(1)}_{ij} = y^{(0)}_{ij} - y^{(0)}_{1i}y^{(0)}_{1j}/y^{(0)}_{11} . \qquad (i,j \neq 1) \qquad (A3.9)_3$$

When they are applied, the variables of the conjugate pair to be interchanged should be moved into first position. Also, the pressure, P, should be treated as $-P$, and the affinity, A, as $-A$, readjusting the notation in the end as needed. Thus, use $G(-P,T,N)$ and $F(V,T,N)$ to find G_{PT} in terms of F. Equation $(A3.9)_2$ then provides

$$G_{(-P)T} = F_{VT}/F_{VV}, \quad . \qquad (A3.9)_4$$

and this gives

$$G_{PT} = -F_{VT}/F_{VV} \qquad (A3.9)_5$$

after readjustment.

A4. THE FUNDAMENTAL EQUATION OF THE IDEAL GAS

This Appendix offers an abbreviated version of the derivation of the fundamental equation of the general ideal gas based on statistical and quantum mechanics.

A4.0 Contents

A4.1 Separability of the Fundamental Equation

The (molar) fundamental equation of the ideal gas in the entropy representation may be written as

$$s = s(u, v) = \mathrm{f}(u) + \mathrm{g}(v)\,. \tag{A4.1}$$

The separability (cf. § 12.1) of $s(u, v)$ into two additive functions, one of which, $\mathrm{f}(u)$, depends only on u while the other, $\mathrm{g}(v)$, depends only on v, results from quantum mechanical considerations. The assumption that the potential energy of interaction of the molecules of an ideal gas does not depend on the distance of the molecules from each other leads to separability of the Schrödinger equation and this, in turn, entails the separability of $s(u, v)$ (Denbigh, 1966).

A4.2 Internal Energy Dependence of the Fundamental Equation

We showed in §§ 12.7 and 12.8 that $\mathrm{f}(u)$ can be expressed as

$$\mathrm{f}(u) = \int_{T_0}^{T} \frac{c_V(T')}{T'}\,\mathrm{d}T' = \int_{T_0}^{T} \frac{c_P(T')}{T'}\,\mathrm{d}T - \mathrm{R}\,\mathit{ln}\,T/T_o \tag{A4.2}$$

where $c_V(T)$ and $c_P(T)$ are the heat capacities of the gas at constant volume, and at constant pressure, respectively. Both depend on the nature of the gas and $\mathrm{f}(u)$ can, therefore, not be written explicitly as a function of u in general.

A4.3 Volume Dependence of the Fundamental Equation

The function $\mathrm{g}(v)$ can be obtained from classical statistical (non-quantum) mechanics. Consider the entropy change in an isothermal expansion of one mole of an ideal gas from v_o to v. This change is given by

$$\mathrm{g}(v) = \mathrm{k}\,\mathit{ln}\,\omega/\omega_o \tag*{(A4.3)$_1$}$$

where k is Boltzmann's constant and ω/ω_o is the number of ways in which the N_{av} molecules[27] in a mole of gas can be distributed over the final volume, v. For a single molecule we would have v/v_o. But the molecules move independently from each other by the basic assumption made for an ideal gas. The thermodynamic probabilities are therefore multiplicative and we have

$$\omega/\omega_o = (v/v_o)^{N_{av}} \,. \qquad \text{(A4.3)}_2$$

Inserting Eq.(A4.3)$_2$ into Eq.(A4.3)$_1$ gives

$$g(v) = N\mathrm{k}\, ln\, v/v_o = \mathrm{R}\, ln\, v/v_o \,. \qquad \text{(A4.3)}_3$$

for the molar entropy of the ideal gas resulting from volume change in the expansion.

A4.4 The Fundamental Equation of the Ideal Gas

Hence, the fundamental equation results as

$$s = s_o + \mathrm{f}(u) + \mathrm{R}\, ln\, v/v_o \qquad \text{(A4.4)}$$

where $\mathrm{f}(u)$ is chosen so that $\mathrm{f}(u_o) = 0$, and, hence, $s_o = s_o''$.

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[27] N_{av} is Avogadro's number.

A5. THE EQUATION OF STATE OF THE IDEAL RUBBER

In § 17.17 we derived the mechanical equation of state of the ideal rubber from the statistical theory of rubber elasticity. It can be derived also by the methods of continuum mechanics. The latter seeks to establish a *constitutive equation* or *material equation of state*, i.e., a relation between the stress tensor and the deformation tensor. The former represents the system of forces applied to the material and the second contains the description of the resulting deformation. Both tensors are symmetric three-dimensional second-order tensors and can, therefore, be expressed as symmetric 3 × 3 matrices. Any such matrix is characterized fully by three invariants, quantities which are independent of any coordinate system chosen to describe the system of forces and/or the deformation.

A5.0 Contents

A5.1 The Invariants of the Deformation Tensor of an Incompressible Rubber

Let λ_i stand for the *extension ratios*, L_i/L_{oi}, where the L_i are the deformed, and the L_{oi} are the undeformed lengths in the three principal directions. The first two invariants of the deformation tensor of an incompressible rubber then become

$$\mathrm{I}_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 = \lambda_1^2 + \lambda_2^2 + \lambda_1^{-2}\lambda_2^{-2} \tag*{(A5.1)$_1$}$$

and

$$\mathrm{I}_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_1^{-2}\lambda_2^{-2} \tag*{(A5.1)$_2$}$$

since the third invariant, because it represents changes in volume, is unity. We have

$$\mathrm{I}_3 = \lambda_1^2\lambda_2^2\lambda_3^2 = 1 \tag*{(A5.1)$_3$}$$

for an incompressible rubber

A5.2 Deformation in Uniaxial Tension of an Incompressible Rubber

Since the rubber is considered to be isotropic, we derive the equation of state by considering uniaxial (also called simple) tension in which a force is applied in one direction and the material is free to contract equally in the two perpendicular directions. We then have $\lambda_1 = \lambda$, and $\lambda_2 = \lambda_3 = \lambda^{-1/2}$, and the two invariants become

$$\mathrm{I}_1 = \lambda^2 + 2\lambda^{-1} \qquad \text{and} \qquad \mathrm{I}_2 = \lambda^{-2} + 2\lambda\,. \tag*{(A5.2)}$$

A5.3 The Elastic Potential or Strain Energy Density of an Incompressible Rubber

Now, by Eq.(17.18)$_1$, at constant temperature and volume the force in uniaxial tension is

$$f = \left.\frac{\partial F}{\partial L}\right|_{T,V} = A_o \frac{\partial F}{V_o \partial(L/L_o)} \qquad (\text{A5.3})_1$$

where $V_o = A_o L_o$ is the initial (undeformed) volume, and F/V_o is the (Helmholtz) free energy of deformation per unit volume. The latter is commonly called the *elastic potential* or the *strain energy density*, W.

The elastic potential is in general a function of the three invariants of the deformation tensor. Since $\mathrm{I}_3 = 1$ for an incompressible rubber, the elastic potential becomes $W = W(\mathrm{I}_1, \mathrm{I}_2)$ and a Taylor expansion in the two invariants yields

$$W = \sum\nolimits_{ij} \mathrm{C}_{ij}\,(\mathrm{I}_1 - 3)^i\,(\mathrm{I}_2 - 3)^j \qquad \mathrm{i,j} = 0,1,2,\ldots \quad (\text{A5.3})_2$$

where the C_{ij} are material constants. $\mathrm{C}_{00} = 0$ because the strain energy density vanishes in the absence of any deformation, i.e. when $\mathrm{I}_1 = \mathrm{I}_2 = 3$. Retaining only the first term in the expansion, we obtain

$$W = \mathrm{C}_{10}\,(\mathrm{I}_1 - 3) = \mathrm{C}_{10}\,(\lambda^2 + 2\lambda^{-1} - 3) \qquad (\text{A5.3})_3$$

for the strain energy density fiunnction of an incompressible rubber.

A5.4 The Constitutive Equation of an Incompressible Rubber

By Eq.(A5.1)$_5$,

$$f = A_o \frac{\partial W}{\partial \lambda} = 2A_o\mathrm{C}_{10}(\lambda - \lambda^{-2})\,. \qquad (\text{A5.4})_1$$

But $F/A_o = \sigma$, where σ is the stress, and $(\lambda - \lambda^{-2})$ is a measure of the strain, in uniaxial tension applied to an isotropic incompressible material. The ratio of stress to strain is a modulus. By identifying $2\mathrm{C}_{10}$ with the (shear) modulus, G, of the material, we write the equation of state as

$$\sigma = \mathrm{G}(\lambda - \lambda^{-2}) \qquad (\text{A5.4})_2$$

and this is the same as the Eq.(17.17)$_2$ derived from the statistical mechanical theory of rubber elasticity.

A6. POSITIVE DEFINITENESS OF A QUADRATIC FORM

This Appendix is concerned with the establishment of the conditions that insure the positive or negative definiteness of a homogeneous quadratic form. This form, and the question of its definiteness, play a crucial role in §§ 18.3 to 18.5 in the context of the criteria of thermodynamic stability. The Appendix makes use of the relations between the second-order partial derivatives of a Legendre Transform that were introduced in § A3.9. The discussion deals with the binary simple system (cf. §§ 18.8 and 18.14)

A6.0 Contents

A6.1 Problem Statement

Given a homogeneous quadratic form

$$\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q} = \sum\nolimits_{ij} y_{ij}^{(0)}\, dx_i\, dx_j \tag{A6.1}$$

we wish to find the conditions that will ensure that it is either positive or negative definite. When $i = j$, $dx_i dx_j$ is necessarily positive. Hence, we must eliminate $dx_i dx_j$ when $i \neq j$. The usual method of diagonalization by eigenvalues does not lead to a useful result because the eigenvalues are devoid of physical meaning. We use Sylvester's method of determinants. By Sylvester's criterion[28] the positive definiteness of a homogeneous quadratic form is guaranteed if all the principal subdeterminants of the matrix **A** are positive definite. The form is negative definite if the matrix $-\mathbf{A}$ is positive definite. Positive definiteness is therefore involved whether the base function is chosen as $y^{(0)} = U$, i.e., in the energy representation, or as $y^{(0)} = S$, i.e., in the entropy representation.

A6.2 The Quadratic Form in the Energy Representation

Given a binary simple system the base function in the energy representation is

$$y^{(0)} = U(S, V, N_{\mathrm{A}})\,. \qquad \text{(A6.2)}_1$$

Using the 'double subscript' notation for second-order partial derivatives (cf. § 18.8) for convenience, simplifying the notation by writing A for N_{A}, and letting dots indicate symmetrical elements, the (non-singular) matrix **A** becomes

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[28] See, e.g., Korn and Korn (1968), p. 420.

$$\mathbf{A} = \begin{vmatrix} U_{SS} & U_{SV} & U_{S\mathrm{A}} \\ \cdot & U_{VV} & U_{V\mathrm{A}} \\ \cdot & \cdot & U_{\mathrm{AA}} \end{vmatrix} . \tag*{(A6.2)$_2$}$$

The three principal subdeterminants of **A** are

$$\Delta_1 = U_{SS} , \tag*{(A6.2)$_3$}$$

$$\Delta_2 = \begin{vmatrix} U_{SS} & U_{SV} \\ \cdot & U_{VV} \end{vmatrix} , \tag*{(A6.2)$_4$}$$

$$\Delta_3 = \begin{vmatrix} U_{SS} & U_{SV} & U_{S\mathrm{A}} \\ \cdot & U_{VV} & U_{V\mathrm{A}} \\ \cdot & \cdot & U_{\mathrm{AA}} \end{vmatrix} . \tag*{(A6.2)$_5$}$$

Expansion of the second subdeterminant yields Δ_2 as

$$\Delta_2 = U_{SS}(U_{VV} - U_{SV}^2/U_{SS}) \tag*{(A6.2)$_6$}$$

and, since

$$U_{VV} - U_{SV}^2/U_{SS} = F_{VV} \tag*{(A6.2)$_7$}$$

by Eq.(A3.9)$_3$, it becomes

$$\Delta_2 = U_{SS}F_{VV} . \tag*{(A6.2)$_8$}$$

Recasting the third subdeterminant in terms of the derivatives of F with the help of Eqs.(A3.9)$_1$ to (A3.9)$_3$ yields

$$\Delta_3 = \begin{vmatrix} -1/F_{TT} & -F_{TV}/F_{TT} & -F_{T\mathrm{A}}/F_{TT} \\ \cdot & -F_{TV}^2/F_{TT} + F_{VV} & -F_{TV}F_{T\mathrm{A}}/F_{TT} + F_{V\mathrm{A}} \\ \cdot & \cdot & -F_{T\mathrm{A}}^2/F_{TT} + F_{\mathrm{AA}} \end{vmatrix} . \tag*{(A6.2)$_9$}$$

We now multiply the first column by $-F_{TV}$ and add the products to column 2. Then, we multiply the first column by $-F_{T\mathrm{A}}$ and add these products to column 3. This leads to

$$\Delta_3 = \begin{vmatrix} -1/F_{TT} & 0 & 0 \\ -F_{TV}/F_{TT} & F_{VV} & F_{V\mathrm{A}} \\ -F_{T\mathrm{A}}/F_{TT} & F_{V\mathrm{A}} & F_{\mathrm{AA}} \end{vmatrix} \qquad (\mathrm{A}6.2)_{10}$$

and, since $-1/F_{TT} = U_{SS}$ by Eq.(A3.9)$_1$, we have

$$\Delta_3 = U_{SS}\, F_{VV}\, (F_{\mathrm{AA}} - F_{V\mathrm{A}}^2/F_{VV})\,. \qquad (\mathrm{A}6.2)_{11}$$

But

$$F_{\mathrm{AA}} - F_{V\mathrm{A}}^2/F_{VV} = G_{\mathrm{AA}}\,, \qquad (\mathrm{A}6.2)_{12}$$

again by Eq.(A3.9)$_3$, and therefore

$$\Delta_3 = U_{SS}\, F_{VV} G_{\mathrm{AA}}. \qquad (\mathrm{A}6.2)_{13}$$

By Sylvester's criterion, then, $\mathbf{q}^{\mathrm{T}}\mathbf{A}\,\mathbf{q}$ will be *positive* definite if U_{SS}, F_{VV}, and G_{AA} are all three > 0. For this to be true we must have

$$\Delta_1 = U_{SS} > 0 \qquad (\mathrm{A}6.2)_{14}$$

$$\Delta_2 = U_{SS} F_{VV} > 0 \qquad (\mathrm{A}6.2)_{15}$$

and

$$\Delta_3 = U_{SS}\, F_{VV} G_{\mathrm{AA}} > 0. \qquad (\mathrm{A}6.2)_{16}$$

The condition that $U_{SS} > 0$ ensures that $F_{VV} > 0$ also, and it follows that $G_{\mathrm{AA}} > 0$.

Letting $\Delta_0 = 1$, the criteria of stability are found from the relation

$$\frac{\Delta_j}{\Delta_{j-1}} = y_{jj}^{(j-1)} > 0\,. \qquad j = 1, 2, 3 \qquad (\mathrm{A}6.2)_{17}$$

Although we have shown the procedure here only for the binary simple system, we can generalize the result to

$$y_{jj}^{(j-1)} > 0 \qquad j = 1, 2, \ldots \mathrm{n}{-}1 \qquad (\mathrm{A}6.2)_{20}$$

when the base function is chosen as $y^{(0)} = U$.

A6.3 The Quadratic Form in the Entropy Representation

Let us now examine under what circumstances $\mathbf{q}^{\mathrm{T}}\mathbf{A}\ \mathbf{q}$ will be *negative* definite when the base function is chosen as

$$y^{(0)} = S(U, V, N_{\mathrm{A}}). \tag*{(A6.3)$_1$}$$

We have

$$\mathbf{A} = \begin{vmatrix} S_{UU} & S_{UV} & S_{U\mathrm{A}} \\ \cdot & S_{VV} & S_{V\mathrm{A}} \\ \cdot & \cdot & S_{\mathrm{AA}} \end{vmatrix} \tag*{(A6.3)$_2$}$$

The quadratic form will be negative definite, if the matrix $-\mathbf{A}$ is positive definite. We therefore recast Eq.(A6.3)$_2$ as

$$-\mathbf{A} = \begin{vmatrix} |S_{UU}| & |S_{UV}| & |S_{U\mathrm{A}}| \\ \cdot & |S_{VV}| & |S_{V\mathrm{A}}| \\ \cdot & \cdot & |S_{\mathrm{AA}}| \end{vmatrix} \tag*{(A6.3)$_3$}$$

where $|S_{UU}|$ is the *absolute value* of S_{UU}, etc.

We now follow a development completely analogous to the one we employed in § A6.2, bearing in mind that when $y^{(0)} = S$, then $y^{(1)} = \Psi$, and $y^{(2)} = \Phi$, where Ψ and Φ are the Massieu functions given by Eqs.(9.1)$_2$ and (9.2)$_1$. We find

$$\Delta_1^{(-)} = |S_{UU}| > 0 \tag*{(A6.3)$_4$}$$

$$\Delta_2^{(-)} = |S_{UU}|\,|\Psi_{VV}| > 0 \tag*{(A6.3)$_5$}$$

and

$$\Delta_3^{(-)} = |S_{UU}|\,|\Psi_{VV}|\,|\Phi_{\mathrm{AA}}| > 0\ , \tag*{(A6.3)$_6$}$$

where the superscript $^{(-)}$ denotes the subdeterminants of the $-\mathbf{A}$ matrix. Since all the subdeterminants are positive definite, the matrix is positive definite also, and it follows that the $-\mathbf{A}$ matrix is *negative* definite. Consequently, since all subdeterminant of the latter matrix must be negative, we must have

$$\Delta_1 = S_{UU} < 0 \tag*{(A6.3)$_7$}$$

$$\Delta_2 = |S_{UU}|\,\Psi_{VV} < 0 \tag*{(A6.3)$_8$}$$

and

$$\Delta_3 = |S_{UU}|\,|\Psi_{VV}|\,\Phi_{AA} < 0. \qquad (A6.3)_9$$

Then stability criteria thus result as $S_{UU} < 0$, $\Psi_{VV} < 0$, and $\Phi_{AA} < 0$. Generalizing these findings as in the preceding section, we obtain

$$y_{jj}^{(j-1)} < 0\,. \qquad j = 1, 2, \ldots, n-1 \qquad (A6.3)_{10}$$

when the base function is chosen as $y^{(0)} = S$.

A7. HEAT CONDUCTION AT THE SYSTEM BOUNDARIES

We consider heat conduction in a one-component, isotropic body under an invariant temperature distribution at its boundaries, and show that *that* part of the rate at which $\Theta(t)$, the rate of entropy production, changes with time because the driving forces change, is negative if the conditions at the boundaries of the system are constant (cf. § 30.2).

Since we are dealing with a pure heat flow, the entropy production is

$$\Phi(t) = \boldsymbol{J}_Q(t) \cdot \boldsymbol{F}_Q(t) = \boldsymbol{J}_Q(t) \cdot \nabla_t(1/T) \qquad (\mathrm{A7})_1$$

where $\boldsymbol{J}_Q(t)$ and $\nabla_t(1/T)$ are the time-varying heat flux and the temperature gradient that drives it. We thus have

$$\frac{d\Theta_F(t)}{dt} = \int_V \boldsymbol{J}_Q(t) \cdot \frac{\partial}{\partial t}\left[\nabla_t\left(\frac{1}{T}\right)\right] dV \qquad (\mathrm{A7})_2$$

and integration by parts yields

$$\frac{d\Theta_F(t)}{dt} = \int_S \left[\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\right] \boldsymbol{J}_Q(t) \cdot d\boldsymbol{S} - \int_V \left[\frac{\partial}{\partial t}\left(\frac{1}{T}\right)\right] [\nabla_t \cdot \boldsymbol{J}_Q(t)]\, dV\,. \qquad (\mathrm{A7})_3$$

Because the temperature does not change with time at the system boundaries, the surface integral is zero. The divergence of the heat flux can be shown[29] to be given by

$$\nabla \cdot \boldsymbol{J}_Q = -\rho c_V \frac{\partial T}{\partial t} \qquad (\mathrm{A7})_4$$

where ρ is the density, and $c_V > 0$ is the (constant) molar heat capacity at constant volume. Because $c_V > 0$, inserting Eq.(A7)$_4$ into Eq.(A7)$_3$ then leads to

$$\frac{d\Theta_F(t)}{dt} = -\int_V \frac{\rho c_V}{T^2}\left(\frac{\partial T}{\partial t}\right)^2 dV \leq 0 \qquad (\mathrm{A7})_5$$

Thus, the rate of entropy production owing to heat conduction under a time-invariant temperature distribution at the boundaries decreases with time until a minimum is reached in a linear steady state.

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[29] Wisniewski et al. (1976), *loc.cit.*

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LIST OF SYMBOLS

Symbols that occur only in isolated instances and are not referred to elsewhere, have not been included in this list. When the physical property denoted by the symbol may occur underr different names, only that preferred in this text is listed. A bold number following an entry indicates the section where the symbol is first introduced or defined.

Roman Letters

A	(de Donder's) Affinity **20.5**
$A_o(\mathrm{T})$	Standard affinity at P_o and T **21.2**
A_o	Inititial (undeformed) area **17.14**
B	$U - TS - fL$ **17.5**
c_j	N_j/V, molar concentration of the jth species **21.3**
c_V	Molar isochoric heat capacity **10.3**
C_V	Isochoric heat capacity **10.1**
$C_{V,L}$	Isochoric heat capacity at constant length **17.6**
c_P	Molar isobaric heat capacity **10.3**
C_P	Isobaric heat capacity **10.2**
$C_{P,f}$	Isobaric heat capacity at constant force **17.7**
$C_{P,L}$	Isobaric heat capacity at constant length **17.8**
d_eS	(Infinitesimal) change in entropy exchanged with the exterior **5.6**
d_iS	(Infinitesimal) change in entropy produced in the interior **5.6**
$d_F\Theta$	(Infinitesimal) change in rate of entropy production due to changes in $\boldsymbol{F}$ **30.1**
$d_J\Theta$	(Infinitesimal) change in rate of entropy production due to changes in $\boldsymbol{J}$ **30.1**
D	$U - fL$ **17.5**
D_j	Coefficient of diffusion of the jth matter species **27.10**
E	Elasthalpy **17.5**
f	Number of degrees of freedom **8.8**
f	Force in simple tension **17.2**
f_s	Entropy contribution to the restoring force in rubber **17.18**
f_u	(Internal) energy contribution to the restoring force in rubber **17.18**
F	Free energy **8.10**
F	Generalized scalar driving force in the entropy production representation **23.4**
$\boldsymbol{F}$	Symbolic notation for a generalized vector driving force in the entropy production representation **23.5**
F	Symbolic notation for generalized tensor driving force in the entropy roduction representation **23.6**
F_i	Indicial notation for a generalized vector driving force in the entropy production representation **23.5**
F_{ij}	Indicial notation for a generalized tensor driving force in the entropy production representation **23.6**
F_N	Diffusional driving force in a discretesystem **28.2**
$\boldsymbol{F}_{N_j}$	Diffusional driving force for the jth matter species **27.2**
$\boldsymbol{F}_Q$	Thermal driving force for the heat flux **27.8**
F_U	Thermal driving force in a discrete system **28.2**
$\boldsymbol{F}_U$	Thermal driving force for the energy flux **27.2**
G	Free enthalpy **8.16**
$\overline{G}_i$	Partial molar free enthalpy of the ith component, **14.6**

H	Enthalpy **8.13**
$\overline{H}_i$	Partial molar enthalpy of the *i*th component **14.10**
I_k	*k*th intensive parameter in the entropy representation **3.4**
J	Grand canonical potential **8.19**
J	Generalized scalar flux **23.4**
$\mathbf{J}$	Symbolic notation for a generalized vector flux **23.5**
$\mathbf{J}$	Symbolic notation for a generalized tensor flux **23.6**
J_k	Indicial notation for a generalized vector flux **23.5**
J_{kl}	Indicial notation for a generalized tensor flux **23.6**
$\mathbf{J}_M$	Mass action flux **27.1**
J_N	Matter flux in a discrete system **28.2**
$\mathbf{J}_{N_j}$	Matter flux of the *j*th species **25.3**
$\mathbf{J}_Q$	Heat flux **27.1**
$\mathbf{J}_S$	Entropy flux **25.4**
J_U	Energy flux in a discrete system **28.2**
$\mathbf{J}_U$	Energy flux **25.2**
$K_c(T)$	Reaction equilibrium constant in terms of the molar concentrations **21.3**
$K_{\bar{n}}(P, T)$	Reaction equilibrium constant in terms of the mole fractions **21.3**
$K_p(T)$	Reaction equilibrium constant in terms of the partial pressures **21.2**
L	Extension in simple tension **17.2**
L_0	Initial (undeformed) length **17.14**
L	(Scalar) phenomenological coefficient **23.4**
$\mathbf{L}$	Symbolic notation for the (tensorial) phenomenological coefficient in the entropy production representation **23.8**
L_{ik}	Indicial notation for the (tensorial) phenomenological coefficient in the entropy producton repre sentation **23.8**
M	Mass action **1.4**
$\bar{n}_i$	*i*th Mole fraction
N	Mole number **2**
N_k	*k*th mole number **2.12**
P	Pressure **3.9**
P_j	Partial pressure of the *j*th component **15.8**
q^*	Heat of transport **28.9**
Q	Heat **2.6**
Q'	Internally generated heat **2.7**
R	Universal gas constant **12.1**
s	Molar entropy **14.1**
s^*	Entropy of transport **28.4**
S	Entropy **2**
$\overline{S}_i$	Partial molar entropy of the *i*th component **14.10**
T	(Thermodynamic) temperature **3.5**
u	Molar internal energy **14.1**
u^*	Energy of transport **28.5**
U	Internal energy **2**
$\overline{U}_j$	Partial molar internal energy of the *j*th component **20.8**
v	Molar volume **14.1**
$\bar{v}_i$	Volume fraction of the *i*th component **16.16**
v	Rate (velocity) of reaction **22.4**
V	Volume **2**
V_0	Initial (undeformed) volume **17.1**
$\overline{V}_i$	Partial molar volume of the *i*th component **14.4**
W	Work **2**
W	Strain energy density **A5.3**
X	Totality of extensive parameters **2.11**
X_k	*k*th extensive parameter **2.11**

$\overline{X}_i$	ith partial molar quantity **14.4**
Y_k	kth intensive parameter in the energy representation **3.3**
z	Molar free elasthalpy **17.10**
Z	Free elasthalpy **17.5**
Z	Generalized scalar driving force in the energy retention representation **26.2**
$\boldsymbol{Z}$	Symbolic notation for a generalized vector driving force in the energy retention representation **24.4**
$\mathbf{Z}$	Symbolic notation for a generalized tensor driving force in the energy retention representation **26.2**
Z_k	Indicial notation for a generalized vector driving force in the energy retention representation

Greek Letters

α_P	Isobaric expansivity **10.2**
$\alpha_{P,f}$	Isobaric expansivity at constant force **17.7**
$\alpha_{P,L}$	Isobaric expansivity at constant length **17.8**
α_S	Adiabatic expansivity **10.1**
$\alpha_{S,L}$	Adiabatic expansivity at constant length **17.6**
$\beta_{P,f}$	Isobaric length-temperature coefficient per unit length at constant force **17.7**
$\beta_{S,V}$	Adiabatic-isochoric length-temperature coefficient per unit length **17.6**
γ	Heat capacity ratio **10.3**
γ_V	Isochoric pressure-temperature coefficient **10.4**
$\gamma_{V,L}$	Isochoric pressure-temperature coefficient at constant length **17.8**
Γ	Massieu function $S[P/T, \mu/T]$ **9.2**
ϵ_e	Efficiency of a heat engine **7.6**
ϵ_p	Coefficient of performance of a heat pump **7.8**
ϵ_r	Coefficient of performance of a refrigerator **7.9**
ε_n	nth component of the strain tensor **17.1**
$\zeta_{T,L}$	Isothermal force-pressure coefficient at constant length **17.8**
Θ	Massieu function $S[\mu/T]$ **9.1**
$\mathit{\Theta}$	Rate of entropy production **22.5**
$\varkappa$	Thermal conductivity **27.9**
κ_S	Adiabatic compressibility **10.1**
$\kappa_{S,L}$	Adiabatic compressibility at constant length **17.6**
κ_T	Isothermal compressibility **10.2**
$\kappa_{T,f}$	Isothermal compressibility at constant force **17.7**
$\kappa_{T,L}$	Isothermal compressibility at constant length **17.8**
λ	Stretch ratio **17.17**
Λ	Latent heat **19.11**
$\mathit{\Lambda}$	Symbolic notation for the (tensorial) phenomenological coefficient in the energy retention representation **24.4**
$\mathit{\Lambda}_{kl}$	Indicial notation for the (tensorial) phenomenological coefficient in the energy retention representation **24.5**
μ	Chemical potential **8.24**
μ_k	kth chemical potential **3.6**
μ_i^*	Chemical potential of the ith pure substance **14.7**
ν_e	Number of moles of effective chains between crosslinks **17.17**
ν_j	jth stoichiometric coefficients **20.2**

ξ	Extent of reaction **20.4**
Ξ	Massieu function $S[P/T]$ **9.1**
Π	Osmotic pressure **16.13**
$\rho_{S,V}$	Adiabatic-isochoric length-force coefficient per unit length **17.6**
$\rho_{T,P}$	Isothermal-isobaric force-length coefficient **17.8**
σ	Stress in simple tension **17.17**
σ_n	nth components of the stress tensor **17.1**
$\varUpsilon$	Energy retention function **24.2**
Φ	Planck function $S[1/T, P/T]$ **9.2**
ϕ	Number of phases **19.16**
$\varPhi$	Entropy production function **24.2**
$\chi_{S,V}$	Adiabatic linear compressibility at constant volume **17.6**
$\chi_{T,f}$	Isothermal linear compressibility at constant force **17.7**
$\psi_{P,L}$	Isobaric force-temperature coefficient at constant length **17.8**
$\varPsi$	Dissipation function **22.7**
Ψ	'THE' Massieu function **9.1**
$\varOmega$	Kramer function $[1/T, \mu/T]$ **9.2**
$\varOmega_j$	jth chemical symbols **20.2**

Operators

d	Exact differential
δ	Inexact differential
∂	Partial differential
Δ	Difference operator
∇	Spatial differential operator
ln	Natural logarithm
sgn	sign of an expression
[ ]	Legendre transform

Superscripts

HR	Heat reservoir **6.4**
MR	Matter reservoir **6.6**
RHS	Reversible heat source **6.3**
RMS	Reversible matter source **6.5**
RWS	Reversible work source **6.1**
VR	Volume reservoir **6.2**
WR	Work reservoir **6.2**

AUTHOR AND SUBJECT INDEX

***Numbers refer to sections, not pages. When the reference is to an author's name, the name is set in capital letters. Search hints: look for* Carnot engine *under* Carnot, *not under* Engine; if you do not find Athermal entropy *under* Athermal, *look under* Entropy.** *A comma at the end of a subentry signifies that the subentry precedes the main entry. Thus, an entry like*

Entropy
athermal,

is to be interpreted as

Athermal entropy

Subentries may be nested.