CBEg 6162- Advanced Chemical Engineering Thermodynamics

Introduction

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CBEg 6162-ADCHENTD-Outline

CHAPTER-1-Introduction to ADCHENTD

- ***Systems***
- ***Boundaries and constraints***
- ***Equilibrium***
- ***Energy***
  - *Kinetic Energy*
  - *Potential Energy*
  - *Internal Energy*
- ***Entropy***

- **Thermodynamics** is a science that includes the study of **energy transformations and of the relationships among the physical properties of substances** that are affected by these transformations.
  - *Definition is **broad and vague.***
  - ***Mechanical engineers** typically focus on **power and refrigeration** devices such as **steam power plants, fuel cells, nuclear reactors, etc.***
  - ***Chemical engineers** typically focus on **phase equilibria and chemical reactions and the associated properties**.*
  - *Element which really sets thermodynamics apart from other sciences is the **study of energy transformations through heat and work.***

- **Thermodynamics** was formalized by ***Joule, Kelvin , Clausius and Carnot in the 19th century Later Gibbs*** developed this into ***a subject of wide applicability***.
- There are ***two different approaches*** in the study of thermodynamic namely ***macroscopic and microscopic***
- Consider a certain amount of gas in a cylinder piston assembly. The volume (v) occupied by the gas, the temperature (T) and pressure (p) of exerted by the gas can be easily measured. The thermodynamic state of that gas can be described by specifying the variables, p, v and T. The approach in ***which only the measurable variables*** are used to describe the state of a system is called ***macroscopic approach(classical).*** In this approach the structure of a matter is not taken in to account and only a few variable are enough to describe the system .

- On the other hand the same gas can be considered as consisting of ***a large number of molecules or atoms*** each of which moves randomly with independent velocity state . Each molecule can be specified in terms of ***three position coordinates*** and ***three velocity coordinates or momentum coordinates***. Alternatively the state of each molecule can be specified in terms of ***its complex wave function $\varphi(x,y,z,t)$*** such a specification constitutes the essence of microscopic approach (statistical) since the position and velocity coordinates of the molecules change with time, as a result of collision with other molecules , the properties of gas changes with time.

- Therefore, the instrument records the time average value of property but not the instantaneous value of a property of the system. To deduce ***the time average properties from the wave function φ(x,y,z,t), statistical mechanics is normally employed***. In ***statistical thermodynamics the microscopic approach*** is adopted.
- The discussion of ***statistical thermodynamics*** can be simplified and can be easy to understand when ***the basics of classical thermodynamics are grasped well***. The most important concepts of ***classical thermodynamics*** like system, ***boundaries, internal, potential, kinetic energies and entropy*** have been given coverage in here.

- In thermodynamics it is a common practice to isolate the subject of interest. The part of area where interest lies upon is called ***a system*** and the part that isolates the system from the rest of the world is called ***boundary.*** For subject of simplicity the system chosen can be taken as ***macroscopically homogenous, uncharged and is not acted by magnetic or gravitational fields***.
- **Thermodynamic system** is a definite quantity of matter enclosed by some boundary.
- **Boundaries and constraints** - A system is separated from its surroundings by a boundary. Depending on the type of the boundary, a system can interact with the surroundings and exchange of mass and energy in the form of work and heat.

Boundaries can be listed as:

- **Adiabatic, rigid and impermeable:-** Such kind of boundary ***isolate a system*** from *exchanging material or expanding or exchanging energy in the form of heat*. And such a body is isolated from the system well.
- **Diathermal, rigid/movable and permeable/impermeable:** - such kind of boundary is *capable of exchanging energy in the form of heat* and also *exchange matter with the environment*. But ***do have/lack*** the capacity to *exchange energy with the environment through expansion and compression.*

- It's possible to manipulate the nature of boundaries so that the system undergoes a change of state. Suppose ***a gas contained in a cylinder –piston assembly is initially in the state (p,v).*** It is desired to expand the gas adiabatically to ***a final volume*** v_2. The adiabatic expansion process can be carried out by replacing *the original rigid, adiabatic and impermeable boundary* by *movable adiabatic and impermeable boundary*. Similarly energy flow in the form of heat can be initiated by replacing an *adiabatic boundary* by *a diathermal, boundary*. The process of division of component j can be initiated by replacing *impermeable boundary* by *a semi permeable boundary which is non restrictive with respect to component j.*

- Another ***important concept*** in thermodynamic is ***equilibrium.*** In nature, *the flow of energy or matter from one system to another system or within a system does not continue to flow endlessly*. This phenomenon creates a situation to *how much energy and matter can flow*. **Equilibrium** is a situation where *two bodies stop interchanging matter or energy macroscopically*. *Equilibrium condition* is possible *if the process is reversible*.
- Once a system is isolated and left to it self it reaches *a state where all properties of the system remains uniform and constant* such a system *does not have any tendency to under go any changes* and is said to be ***in state of equilibrium***. **Equilibrium** is the concept associated with *the absence of any tendency for any spontaneous change to take place.*

Chapter 1. Criteria for thermodynamic equilibrium

- If the ***two given system*** are ***in state of thermal equilibrium***, which is the criteria for *thermal equilibrium*
- Criteria for ***mechanical equilibrium*** is ***the equality of pressure*** between the two interacting systems.
- The criteria for ***chemical equilibrium*** is the equality of ***chemical potential.***
- A system which ***satisfies simultaneously, thermal, mechanical, and chemical equilibrium is said to be in state of thermodynamic equilibrium***. Since the properties are *uniform throughout the system in state of equilibrium*, a single value can be specified to each property.

- ***Thermodynamics*** is ***energy in transition***, on the other side the *basics of thermodynamics* is concerned in an important concept called ***energy***. Energy is defined as ***capacity to do work***. And different forms of energy exist which each of them have different characteristics and according to that, they have been given different category.

- ***Kinetic energy-*** when a force F acts on a body of mass, m , the acceleration of the body can be estimated by the application of Newton's second law of motion, F=ma. If the body moves a distance dL, during a small time interval dt, then the work done by the force on the body is given by;

$$dW = FdL = madL = m(\frac{dV}{dt})dL = mdV(\frac{dL}{dt}) = mVdV$$

- if the initial and final velocity of the body are V1 and V2, then the total work done on the body is given by;

$$W = \int FdL = \int_1^2 mVdV = \frac{1}{2}m(V_2{}^2 - V_1{}^2) = \Delta(KE)$$

- All matter possesses *kinetic energy by virtue of its motion* and this can be computed in terms of *the macroscopically measurable quantities*. The kinetic energy possessed by a body can be completely converted into work.

- Potential energy- if a body of mass, m, is moved from an initial elevation Z_1 to a final elevation Z_2 in gravitational field, the force acting on the body is , mg, where, g is the acceleration due to gravity. The work done by the force on the body is given by;

$$W = F(Z_2 - Z_1) = mg(Z_2 - Z_1) = \Delta(PE)$$

- All matter possesses ***potential energy by virtue of its location*** and the potential energy of the body can be determined in ***terms of the macroscopically measurable quantities***. The potential energy possessed by a body can be completely converted into work.

- **Internal energy-** Internal energy is a form associated to ***a microscopic level of a substance or compound***. The particles of atom or molecule which give rise to a substance or a compound are in continuous motion and are never at rest. The ***energy associated to the smallest part***, ***molecules and atoms***, is called ***internal energy.***
- All matter consists of a large number of atoms or molecules and these are in a continuous motion and are never at rest. *The KE associated with translational motion is called (TE).* The energy associated with a rotation of molecules (diatomic and polyatomic) is called (RE). The energy associated with vibration of molecules (polyatomic back-forth about their center of mass) is called (VE).

- The molecules in matter are held together by molecular binding forces and hence certain amount of potential energy is associated with these intermolecular forces. Unlike the K.E and P.E terms; it is not possible to determine the ***RE, TE and VE, as a function of macroscopically measurable quantities.*** ***These energies are associated with the internal structure of the molecule***. The energy possessed by the matter due to internal modes of motion is called internal energy (u) of a matter. This internal energy is highly disorganized form of energy which K.E and P.E are organized form. ***The major task of an engineer is to find means of converting the disorganized form of energy into organized form.***

- Thermodynamic is originated as result of man's continuous effort to convert the ***disorganized form of energy (internal energy of matter) into organized form of energy (work).*** Consequently greater emphasis was laid on ***the development of heat engines***. As a result, the development of ***classical thermodynamics*** was largely based on ***the heat engines and their performance***.
- ***The laws of thermodynamics*** are based on logical reasoning and they were deduced from ***a large number of experimental observations***. Now days, ***thermodynamics*** is widely used not only by mechanical engineers but also by ***chemical engineers,*** metallurgical, engineers, aero space engineers etc. Find wide applications almost in ***all physical and chemical sciences.*** The situation encountered in all these branches of study is such that it is impossible to relate them to heat engines. In the conventional treatment of classical thermodynamics the essential principles are presented through ***the four laws (zero, 1st, 2nd, and 3rd) of thermodynamics.***

- The **laws of thermodynamics** describe some of the fundamental truths of thermodynamics observed in our Universe. Understanding these laws is important to students because many of the processes studied involve the flow of energy.
- **Zeros law of thermodynamics** which says that *when a body A is in thermal equilibrium with a body B*, and *also separately with a body C*, ***then B and C will be in thermal equilibrium with each other.***
- First law of thermodynamics states that the transfer of heat and the performance of work may both cause the same effect in a system. Heat and work are different forms of the entity, called energy, which is conserved; it is about the law of conservation of energy.
- The field of thermodynamics studies the behavior of energy flow in natural systems. From this study, a number of physical laws have been established.

- ***The first law of thermodynamics*** is often called the ***Law of Conservation of Energy***. This law suggests that energy can be transferred from one system to another in many forms. However, it can not be ***created*** nor ***destroyed***. Thus, the total amount of energy available in the Universe is constant. Einstein's famous equation (written **below**) describes the relationship between ***energy and matter:***

$$E = mc^2$$

- In the equation above, energy (E) is equal to matter (**m**) times the square of a constant (c**).** Einstein suggested that ***energy and matter are interchangeable***. His equation also suggests that ***the quantity of energy and matter in the Universe is fixed***.

- Heat can never pass spontaneously from a colder to a hotter body. As a result of this fact, natural processes that involve energy transfer must have one direction, and all natural processes are irreversible. *This law also predicts that the entropy of an isolated system always increases with time*. Entropy is the measure of the disorder or randomness of energy and matter in a system. Because of the second law of thermodynamics both energy and matter in the Universe are becoming less useful as time goes on. Perfect order in the Universe occurred the instance after the Big Bang when energy and matter and all of the forces of the Universe were unified.

- Theory that suggests that about 15 billion years ago all of the matter and energy in the Universe was concentrated into an area smaller than an atom. At this instant, matter, energy, space and time did not exist. Then suddenly, the Universe began to expand at an incredible rate and matter, energy, space and time came into being. As the Universe expanded, matter began to coalesce into gas clouds, and then stars and planets. Some scientists believe that this expansion is finite and will one day cease. After this point in time, the Universe will begin to collapse until a Big Crunch occurs. Big crunch means Collapse of the Universe into its original form before the Big Bang. At the end of this process matter, energy, space, and time will not exist

- ***The third law of thermodynamics*** states that ***if all the thermal motion of molecules (kinetic energy) could be removed***, a state called absolute zero would occur. Absolute zero results in a temperature of 0 Kelvin or -273.15° Celsius.
- The Universe will attain absolute zero when ***all energy and matter is randomly distributed across space***. The current temperature of empty space in the Universe is about 2.7 Kelvins.

- **Entropy (s)**- ***is an important property in thermodynamics***. When a system undergoes a change from initial state 1 to the final state 2 during a given process, the change in entropy of the system is given by

$$\Delta S = S_2 - S_1 = \int_1^2 ds = \int_1^2 \left(\frac{dQ}{T}\right)_R$$

- where *S_1 and S_2 refer to a entropy of the system*. In states 1 and 2 respectively and *dQ is the amount of heat transferred* as a heat at temperature T during a reversible process by which the system is taken from the initial state to a final state.

- Since *entropy is a property of the system the change in its value is independent of the path followed by the system in reaching the final state from the initial state*, therefore If a system undergoes an irreversible process in which it changes from the initial state 1 to the final state 2 the energy change remains the same as if it were to under go the reversible process. The combination of a system and its surrounding constitutes universe and the S of the universe must satisfy the condition that $$(\Delta S)_{system} + (\Delta S)_{surrounding} = (\Delta S)_{universe}$$
- The entropy of the universe can either increase or remain the same but cannot decrease, if the process undergone by the system is reversible. The entropy of the universe remains constant, if the process undergone by the system is reversible and the entropy of the universe increases if the system is irreversible.

Examples

Example 1

- A reversible heat engine shown in Fig. operates with three constant temperature reservoirs at 300K, 600K, and 1200K. It observes 2.4 MJ energy as heat from the reservoir at 1200K and delivers 0.9 MJ energy as work. Determine the heat interaction with the other two reservoirs and the efficiency of the engine which is defined as the ratio of the net work to the energy absorbed as heat.

Example 2

- Two identical bodies of mass '*m*' and a specific heat capacity '*c*' are initially at temperature *T1 and T2*. Determine the maximum amount of work that can be obtained if a heat engine is operated between these two bodies

Examples

Example 3

- An insulated vessel contains 1 Kg supercooled liquid water at *-100C*. If a small crystal of ice of negligible mass is added as a seed to initiate the freezing of water, calculate the mass of the ice formed and the change in the entropy associated with the process of freezing. The specific heat capacity of water is 4.2 kJ/kg K and the latent heat of fusion of water at 00C is 333.4 kJ/kg.

Example 4

- Potable water is produced by condensing steam, generated from saline water, in a heat exchanger. Suppose 1000 kg/h steam at 0.1 Mpa and 1500C enters a heat exchanger and emerges as water at 45 0C. For this purpose cooling water enters the exchanger at 25 oC and leaves at 40 0C. A young engineer claims that he/she devised a device which does the same job as the heat exchanger, and he/she further claims that his/her device not only requires less amount of cooling water but also delivers some net work. The inlet and outlet conditions of cooling water and steam in the new device are identical to that of the heat exchanger. Based on thermodynamic grounds judge whether such a device is feasible. If feasible, determine the saving in cooling water requirement and the power delivered by the device.

- ***Thermodynamic properties*** can be studied either by studying ***macroscopic or microscopic behavior of matter.***
  - **Classical thermodynamics** treats matter *as a continuum and studies the macroscopic behavior of matter*
  - **Statistical thermodynamics** studies the statistical behavior of *large groups of individual particles.* It postulates that *observed physical property behavior (e.g., T, p, V...) is equal to the appropriate statistical average of a large number of particles.*

- **Thermodynamics** is based upon ***experimental observation.***
  - Conclusions of observations have been cast as ***postulates or laws.***
  - Our study of thermodynamics will consider ***five laws or postulates***; ***two dealing with energy transformation*** and ***three dealing with properties***.

- **Energy Transformation Laws:**
  - **First Law of Thermodynamics-**-Energy is conserved. (You can't win!)
  - **Second Law of Thermodynamics-**-Takes many forms. In essence it says that energy has different "quality" and processes only spontaneously proceed in one direction. It isn't possible to convert all of the energy of a system into work. (You can't even break even!)

- **Property Relationship Laws:**
  - **Zeroth Law of Thermodynamics-**-When each of two systems is in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.
  - **Third Law of Thermodynamics-**-The "entropy" of a perfect crystal is zero at absolute zero temperature.
  - **State Postulate-**-The state of a simple, single phase thermodynamic system is completely specified by two independent variables, intensive properties.
- **Energy Conversion and Efficiency**
  - A primary concern in thermodynamics is energy conversion and a measure of energy conversion success is called the efficiency. For energy consuming or producing devices it is called the thermal efficiency: $\eta_{th} = \dfrac{\text{energy desired}}{\text{energy paid for}}$

- Thermodynamic System – is three dimensional region of space bounded by arbitrary surfaces (which may be real or imaginary and may change size or shape) which delineate the portion of the universe we are interested in.
  - **Closed System** is a system that is closed with respect to the flow of matter, e.g., fixed, closed volume. A closed system is defined by a fixed quantity of mass.
  - **Open System** is a system that is open with respect to the flow of matter such as a compressor. The system is defined by an imaginary volume surrounding the region of interest. The surface of this volume is called the control or sigma (s) surface. Mass, heat, work and momentum can flow across the control surface.
  - **Isolated System** is a system that is not influenced in any way by the part of space which is external to the system boundaries. No heat, work, mass or momentum can cross the boundary of an isolated system. (N,V,U) are fixed and constant in a closed system
  - **Simple System** is a system that does not contain any internal adiabatic, rigid and impermeable boundaries and is not acted upon by external forces.
  - **Composite System** is a system that is composed of two or more simple systems.

- ***Property is characteristic of a system.***
  - **Primitive Property** is a property that can in principle be specified by describing an operation or test to which the system is subjected. Examples include mechanical measurements (e.g., pressure, volume, and thermometric temperature T) and heat capacity.
  - **Derived Property** is a property that is mathematically defined in terms of primitive properties.
  - **Intensive Property** is a property that is independent of the extent of or mass of the system. Examples are T, P, density, (x), etc.
  - **Extensive Property** is a property whose value for the system is dependent upon the mass or extent of the system. Examples are the enthalpy, internal energy, volume, etc.
  - **Specific Property** is an extensive property per unit mass. Specific properties are intensive.
  - **State Property** is a property that only depends on the thermodynamic state of the system, not the path taken to get to that state.

Chapter 1. Chapter Summary-State of a system

- **Thermodynamic State**--The condition of the system as characterized by the values of its properties.
- **Stable Equilibrium State** is a state in which the system is not capable of finite spontaneous change to another state without a finite change in the state of the surroundings. Many types of equilibrium must be fulfilled -- thermal, mechanical, phase material and chemical.
- **State Postulate**: The equilibrium state of a simple closed system can be completely characterized by two independently variable properties and the masses of the species contained within the system.

- ***Thermodynamic process is transformation from one equilibrium state to another.***
  - **Quasi-static Process** is a process where every intermediate state is a stable equilibrium state.
  - **Reversible Process** is one in which a second process could be performed so that the system and surroundings can be restored to their initial states with no change in the system or surroundings.
  - ***Reversible processes are quasi-static but quasi-static processes are not necessarily reversible***. A quasi-static process in a simple system is also reversible.
  - ***Irreversibility*** is in contrary when it is not possibly to gain the original situation. But the important thing is when a system undergoes a change from 1 to 2 it is possible to treat it as a reversible process for the irreversible process too.
  - Some factors which render processes irreversible are friction, unrestrained expansion of gasses, heat transfer through a finite temperature difference, mixing, chemical reaction, etc.