CBEg 6162- Advanced Chemical Engineering Thermodynamics

Postulates and equilibrium criteria

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CHAPTER-2-Postulates and equilibrium criteria

- *State of a Systems*
- *Fundamental Problems*
- *Postulates*
- *Intensive parameters and Equations of State*
- *Criteria of Equilibrium*

- The development of ***classical thermodynamics*** was largely based on the ***heat engines and their performance.***
- In ***the conventional treatments of classical thermodynamics,*** the essential principles are presented through ***four laws*** of thermodynamics.
- The study of ***classical thermodynamics*** through ***the postulation approach is a recent development*** and it is gaining wide acceptance.
- It is found to be logically sound and provides ***a better understanding*** of the principles of thermodynamics ***without depending upon the Carnot cycle.***

State of a system

- *Criteria for equilibrium* is necessary to characterize ***the state of thermodynamic system.*** The equilibrium state of a thermodynamic system can be described by specifying its ***internal energy (U) volume (V) and the mole numbers*** of the constituent species (N1,N2,…Nc).

Fundamental problems in Thermodynamics

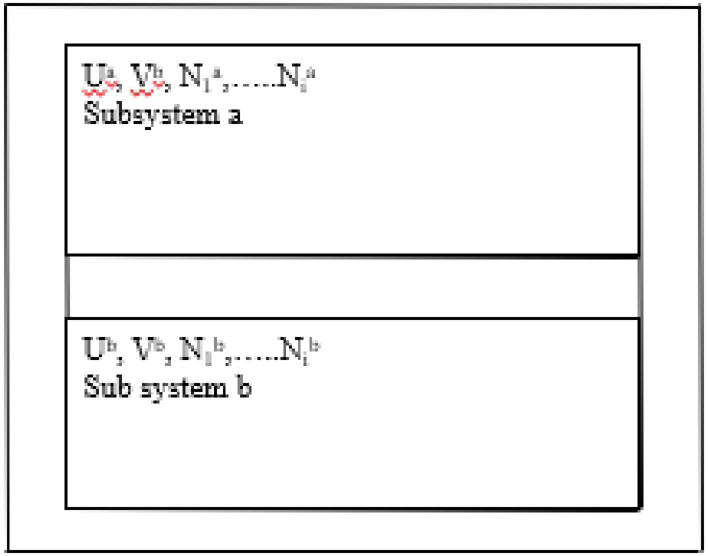
- In ***thermodynamics analysis of processes*** we are interested in determining the change in ***the energy and other properties of the system*** when it interacts with its surroundings or another system.
- Almost all problems in thermodynamics can be reduced to the following fundamental problem. If two given thermodynamic systems in their specified initial states are allowed to interact with each other:-
    - *What will be **the resulting equilibrium state?** and*
    - *What are the **values of the extensive parameters** of the systems in that state?*
    - *The solution to the fundamental problem was **formulated through postulate.***

Fundamental problems in Thermodynamics

- Consider ***an isolated composite system*** consisting of two ***subsystems a and b*** which are separated from each other by ***a rigid, adiabatic and impermeable boundary.***
- Let ***U0a, V0b, Na1,0,…..Nai,0*** represent ***the initial internal energy, volume, and constituent mole number*** 1,2,3..i of system a.
- Similarly ***U0b, V0b, N0b,…..Ni,0b***.represent ***the initial internal energy, volume and constituent mole*** of system b.

Fundamental problems in Thermodynamics

- The ***removal of each constraint initiates*** a spontaneous process leading to ***variation in the value of U,V, N…..Ni*** each subsystems.
- Then it requires to determine the ***values of Ua, Vb, N1a,…..Nia Ub, Vb, N1b,…..Nib. in the final equation state.***



Postulates

- Solution to the fundamental problem in thermodynamics is formulated ***through a set of postulates,***
- In the development of these postulates the central idea is ***to find a simple formal solution to the fundamental problem.***
- The problem deals with ***the determination of the final equilibrium state.***
- Some function of the independent variables, which are used to describe ***the state of the system***, should reach an extremum value when the system attains **a state of equilibrium.**

Postulates -1-

- *This postulate states that the equilibrium-state of a thermodynamic-system is* ***completely characterized by extensive variables U, V, N1… Nc. The entropy (S) of such a system*** *is a function of these variables and, in the* ***absence of internal constraints****, the variables assume such values as* ***to maximize the entropy*** *over all possible constrained equilibrium states.*
- *This postulate states that the equilibrium state of a thermodynamic system is* ***completely characterized by internal energy, volume, and the mole numbers*** *of the constitutes of the system*

Postulates -2-

- *The **entropy of the system increases monotonically with increasing internal energy** and is **equal to zero in the state where** $\left(\frac{\partial U}{\partial S}\right)_{VN_i} = 0$ The entropy is **additive and a continuous and differentiable function.***
- *This postulate states that **the entropy of a system increases with increasing internal energy**. That is* $\left(\frac{\partial S}{\partial U}\right)_{VN_i} > 0$
- *It will be shown that the temperature is defined by the relation*

$$\left(\frac{\partial S}{\partial U}\right)_{VN_i} = \frac{1}{T}$$

Example 1

- *Consider **an isolated composite system consisting of two subsystems a and b** which are separated from each other by **a rigid, adiabatic and impermeable boundary**. The initial values of the extensive parameters in these subsystems are **Ua = 7.2 MJ, Va = 1m3, Na = 1 kmol, Ub = 7.2 MJ; Vb = 1m3, Nb = 2 kmol**. If the internal boundary is made **diathermal**, **determine the final state of equilibrium**. The fundamental relation **S = K(UVN)1/3** where S is in kJ/K; N in kmol, V in m3 and U in kJ and K is a constant with appropriate dimensions, is valid for both the subsystems.*

Intensive Parameters and equation of states

- The relations which ***express the intensive parameters as a function of the independent extensive parameters*** are called ***equation of state***.
- An equation of state is ***a homogeneous zero order function*** of the extensive parameters.
- The ***fundamental relation in the entropy*** representation is given by ***S = S (U.V. N1, N2… Nc)*** and the ***set U, V, N1, N2… Nc*** are called ***the extensive parameters in the entropy representation***. The intensive parameters and the equations of state in the entropy representation are given by

Entropy Representation

$$\left(\frac{\partial S}{\partial V}\right)_{U,V,N_1,\ldots N_c} \equiv \frac{P}{T} = \frac{P}{T}(U,V,N_1,N_2\ldots N_c)$$

$$-\left(\frac{\partial S}{\partial Ni}\right)_{U,V,Nj} \equiv \frac{\mu_i}{T} = \frac{\mu_i}{T}(U,V,N_1,N_2\ldots N_c)$$

The differential of S is given by

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^{c}\frac{\mu_i}{T}dN_i$$

Energy Representation

The fundamental relation in the energy representation is given by

$$\mathbf{U = U(S,\ V,\ N_1,\ N_2\ldots\ N_c)}$$

and the set of variables S, V, N_1, N_2… N_c are called ***the extensive parameters in the energy representation****. The intensive parameters and the equations of state in the energy representation are given by*

$$\left(\frac{\partial U}{\partial S}\right)_{V,N_1,\ldots N_c} \equiv T = T\left(S,V,N_1,N_2\ldots N_c\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,V,N_1,\ldots N_c} \equiv P = P\left(S,V,N_1,N_2\ldots N_c\right)$$

$$-\left(\frac{\partial U}{\partial Ni}\right)_{S,V,Nj} \equiv \mu_i = \mu_i\left(S,V,N_1,N_2\ldots N_c\right)$$

The differential of U is given by $$dU = TdS - PdV + \sum_{i=1}^{c} \mu_i dN_i$$

Example 2

The fundamental relation for a particular thermodynamic system is given by ***U = CS3/NV*** *where C is a positive constant.*

a) *Obtain the* ***three intensive parameters T, P and μ*** *and write the* ***three equations of state*** *of the system*

b) *Show that the three equations of state are* ***homogenous functions of zeroth order***

c) *Express* ***μ as a function of T and P***

Criteria of Equilibrium

- For the system to be in ***a state of thermodynamic equilibrium*** it should simultaneously satisfies ***the criteria of thermal, mechanical and chemical equilibrium.***
- Consider ***an isolated composite system***, consisting of two subsystems a and b, the sub-system are separated from each other by ***a rigid adiabatic and impermeable boundary***. The subsystem a is characterized by $\boldsymbol{U^a, V^a, N^a}$ and the subsystem b is characterized by $\boldsymbol{U^b, V^b, N^b}$.

Thermal Equilibrium

- If the internal boundary is made ***diathermal***, ***energy flow in the form of heat between the two subsystems*** till a state of thermal equilibrium is established.
- Since the internal boundary is ***rigid, diathermal and impermeable***, it is ***restricted*** with respect to ***volume and mole numbers of the constitute species*** but allows the ***exchange of energy*** in the form of heat.

Thermal Equilibrium

- However, the composite system is ***isolated*** and hence ***the total energy of the composite system remains constant***.
- In state of ***thermal equilibrium***, ***the temperature of subsystem a*** must be identical to ***the temperature of subsystem b***. Hence ***the criteria for thermal equilibrium*** is given by

$$\frac{1}{T^a} = \frac{1}{T^b}$$

Example 3

- Consider **an isolated composite system consisting of two subsystems a and b** which are separated from each other by **a rigid, adiabatic and impermeable boundary**. The extensive parameters of the subsystems are **Ua = 7.2 MJ, Va = 1m3, Na = 1 kmol, Ub = 7.2 MJ; Vb = 1m3, Nb = 2 kmol**. The fundamental relation **S = K(UVN)1/3** where S is in kJ/K; N in kmol, V in m3 and U in kJ and K is a constant with appropriate dimensions, is valid for both the subsystems. If the internal boundary is made **diathermal**, **determine the final equilibrium values of Ua, Ub and temperature. Assume K= 6*105.**

Mechanical Equilibrium

- If the internal boundary is made ***movable and diatermal*** the composite system eventually settles into ***a new state of equilibrium***. The internal boundary ***allows the exchange of volume*** and ***energy between the two subsystems***.
- However, ***the total volume and energy of the composite*** system ***remains constant***.
- ***In state of mechanical equilibrium***, ***the pressure of subsystem a must be identical to the pressure of subsystem b***. Hence the criteria for mechanical equilibrium is given by $\frac{P^a}{T^a} = \frac{P^b}{T^b}$

Example 4

- *Consider* ***an isolated composite system consisting of two subsystems a and b*** *which are separated from each other by* ***a rigid, adiabatic and impermeable boundary****. The extensive parameters of the subsystems are* ***Ua = 7.2 MJ, Va = 1m3, Na = 1 kmol, Ub = 7.2 MJ; Vb = 1m3, Nb = 2 kmol****. The fundamental relation given below with R = 8.314 kJ/kmol K is valid for both the systems.*

  S = (N/No)*So + NR In [(U/Uo)3/2 V/Vo(N/No)-5/2]

  Where So = 5/2 NoR – No(μ/T)o.

  Uo, Vo, No, (μ/T)o refer to the parameters of a fictitious state

  If the internal boundary is made ***diathermal and movable****,* ***determine the final equilibrium values of Ua, Va, Ub Vb, temperature and pressure.***

Chemical Equilibrium

- If the internal boundary is made ***diatermal and semi- permeable*** which permit ***the transfer of constituent 1 only and does not allow the transfer of other constitute***, the composite system settles in to a new state of equilibrium.
- Since the internal boundary is ***diatermal and semi-permeable***, it allows ***the exchange of internal energy and the mole number of constitute 1 only between the two sub systems***, but ***does not allow*** the transfer of other constitutes through it.

Chemical Equilibrium

- Moreover as the composite system is ***isolated the total energy and the total mole numbers of constitute 1 should be constant***.
- ***In state of chemical equilibrium***, ***the chemical potential of subsystem a*** must be identical to ***the chemical potential of subsystem b***. Hence the criteria for chemical equilibrium is given by

$$\frac{\mu_i^{\,a}}{T^{\,a}} = \frac{\mu_i^{\,b}}{T^{\,b}}$$

Example 5

- ***An isolated composite system consisting of two subsystems a and b.*** *Initially the subsystems are separated from each other by* ***a rigid, adiabatic and impermeable boundary****. If the internal boundary is made* ***diathermal and semipermeable which allows the transfer of constituent 1 only****,* ***determine the values of Ua, Ub, N1a, N1b and T in the final state of equilibrium****. Assume that both the subsystems a and b obey the fundamental relation for a binary mixture given by*

$$S = (N1+N2)R\ In\ [U3/2V(N1+N20\text{-}5/2] - N1R\ In\ N1/(N1+N2) - N2R\ In\ N2/(N1+N2) + (N1+N2)CK(UV/N)1/3$$

- *where R =8.314 kJ/kmol K and C is an unknown constant. The subscripts 1 and 2 denote the constituents.*