Lectures Note

on

METALLURGICAL THERMODYNAMICS & KINETICS

(MME 202)

B.Tech, 3rd Semester

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DISCLAIMER

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CHAPTER-1
INTRODUCTION TO THERMODYNAMICS

1.1 THERMODYNAMICS:

It is the subject which dealing with the relation between heat and motion. Development of metallurgical Thermodynamic occurs due to the application of chemical thermodynamics to the metals & materials which later on known as Thermodynamics of materials.

1.1.1 Importance of Thermodynamics:

1. It gives the idea about feasibility of the process.
2. It gives the idea about end product & its stability.
3. It is useful in calculation of heat values.

Let us consider a reaction,

$$A + B \rightarrow C + D$$

Then thermodynamically, it can be represented in terms of energy as in following **Fig – 1.1.**

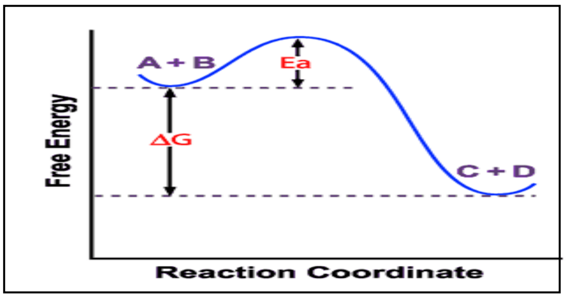

Fig. 1.1: Free energy vs Reaction coordinate diagram for above reaction

1.1.2 Definition of Thermodynamic Terms:

1.1.2.1 System: It is defined as any portion of the universe or the quantity of matter that chosen separately from the rest of the universe & closed by boundary surface.

Types of System: Depending on various parameters system can be classified as follows

(i) Nature of Interaction

- Open system: Both heat & mass transfer possible.
- Closed system: Only heat transfer possible.
- Isolated system: Neither heat nor mass transfer possible.

(ii) Number of components

- Unary component system: System consists of single component
- Multi component system: System consists of more than one component.

(iii) Reactivenes

- Reactive system: System is chemically reactive.
- Non-reactive system: System is chemically non-reactive.

(iv) Phase

- Homogeneous system: System consists of single phase.
- Heterogeneous system: System consists of more than one phase.

1.1.2.2 **Surrounding:** Except the system the rest of the universe is known as surrounding.

The fig – 1.2 is showing how system and surrounding separated by a boundary layer and also different showing what are different interactions involved in it.

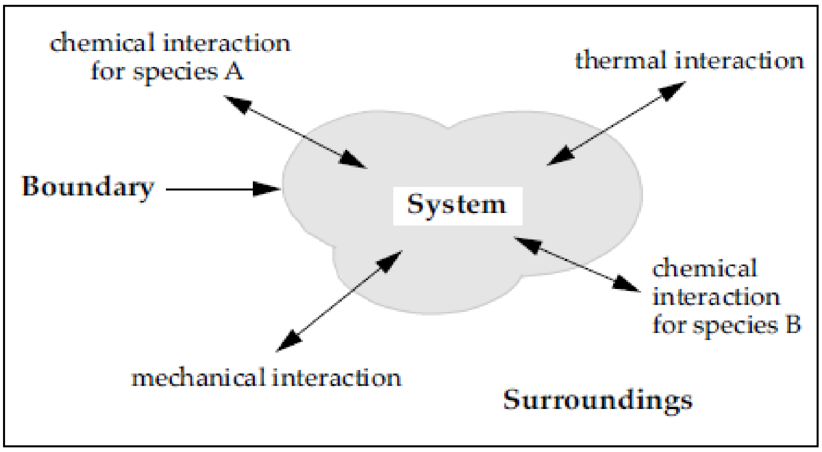

Fig. 1.2: System and surrounding separation by boundary layer

1.1.2.3 Boundary Wall:

This is the wall which separated system from the surrounding.

i. Adiabatic Wall: Not allow to any transparent.
ii. Diathermic Wall: Allow to any transparent.

1.2 PROCESS:

When in a system there is two or more than two parameters get changed then it is known as system gets changed and process occurs.

i. **Cyclic Process:** Sequence of processes which return back to its initial point.

ii. **Adiabatic Process:** Process in which net heat change (Δq) is equal to zero.

iii. **Isothermal Process:** Process in which net temperature change (ΔT) is equal to zero.

iv. **Isobaric Process:** Process in which net pressure change (ΔP) is equal to zero.

v. **Isochoric Process:** Process in which net volume change (ΔV) is equal to zero.

vi. **Quasi-static Process:** It is the process in which every small steps are in equilibrium, so that entire process is in equilibrium.

1.3 PROPERTY:

Generally properties (or state variables) are either extensive or intensive.

i. **Extensive Property:** The properties which depends on the size or mass of the system.
Example: Mass, Area, Volume, Length, Entropy, Enthalpy etc.

ii. **Intensive Property:** The properties which independent of size or mass of the system.
Example: Density, Specific volume, Molar volume etc.

1.4 EQUATION OF STATES:

Equations which depend on the state variables like P, V, T, n are known as equation of states.

i. **Universal Gas Law:** $\mathrm{PV = nRT}$ (1.1)

ii. **Dieterici Model:** $\mathrm{P(V_m - b) = RT\exp(\frac{-a}{V_m RT})}$

(1.2)

iii. **Barthelot Model:** $\mathrm{\left(P + \frac{a}{TV_m^2}\right)(V_m - nb) = nRT}$

(1.3)

[Where

$\mathrm{V_m}$ – Molar volume, $\mathrm{P_c}$ – Critical pressure,

$\mathrm{V_c}$ – Critical volume, $\mathrm{T_c}$ – Critical temperature

a, b – Empirical parameters

$\mathrm{a = 0.4275\frac{R^2T_c^{2.5}}{P_c}, b = 0.0867\frac{RT_c}{P_c}}$]

1.5 SIMPLE EQUILIBRIUM:

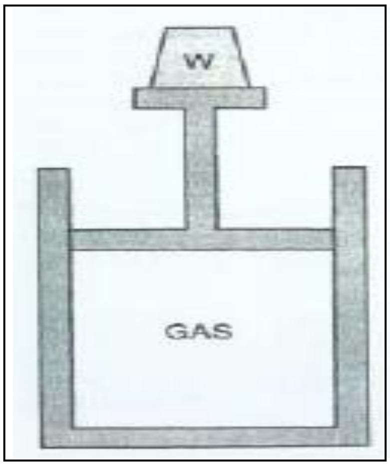

Fig – 1.3: A quantity of gas contained a cylinder with a piston

Above figure 1.3 represents particularly a simple system which consists of a fixed amount of gas in a cylinder by a movable piston and top of the piston a weigh block having weight 'W'. At equilibrium

1. Pressure exerted by the gas on the piston = Pressure exerted by the piston on the gas.
2. Temperature of the gas = Temperature of the surrounding.

(Provided the heat can be transport through the wall of the cylinder)

Case – 1: Let us consider the weight (W) above the piston get decrease, then the pressure on the gas get decrease as a result the gas inside the cylinder get expands by push up the movable piston.

- Temperature (T_1) remains constant.
- Pressure changes from P_1 to P_2.
- Volume changes from V_1 to V_2.

So we have got

Initial state (P_1, V_1, T_1) to Final state (P_2, V_2, T_1).

Case – 2: Now if thermodynamically the temperature of the surrounding get raised from T_1 to T_2. Then heat at the surrounding gets raised. As a result, the flow of heat from the surrounding to the inside of the cylinder occurs.

- Pressure (P_2) remains constant.
- Temperature changes from T_1 to T_2.
- Volume changes from V_2 to V_3.

So we have got

Initial state (P_2, V_2, T_1) to Final state (P_2, V_3, T_2).

From the above case-1 & 2 we have

$$(P_1, V_1, T_1) \xrightarrow{\hspace{2cm}} (P_2, V_2, T_1) \xrightarrow{\hspace{2cm}} (P_2, V_3, T_2)$$

1.6 THERMODYNAMIC EQUILIBRIUM:-

If in a system both thermal & mechanical equilibrium exists simultaneously. Then it is known as in thermodynamic equilibrium.

i. **Thermal Equilibrium:** Uniform temperature throughout the system.
ii. **Mechanical Equilibrium:** Uniform pressure throughout the system.
iii. **Chemical Equilibrium:** Uniform chemical potential throughout the system.

1.7 INTERNAL ENERGY:

It is defined as the inbuilt energy that responsible for the existence of the matter.

Characteristics:

i. It depends on state variables P, T, V, n.
ii. It is a state property and since the state of internal energy is same as the state of the dependent parameters. So it is known as single valued function.
iii. Internal energy is the sum of the energy associated with translation motion, vibration motion and electronic configuration.
iv. For a cyclic process, change in internal energy (**Δ**U) becomes zero.
v. Internal energy is perfect differential i.e. $U_i = f(P_{i,}V_{i,}T_i)$
    a. At constant temperature,

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial V}\right)_P dV = f(V, P)_T$$

    b. At constant volume, $\Delta U = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT = f(P, T)_V$
    c. At constant pressure, $\Delta U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = f(V, T)_P$

1.8 PHASE DIAGRAM / CONSTITUTION DIAGRAM:

Phase: It is defined as a finite volume in the physical system within which the properties are uniformly constant i.e. do not experience any abrupt change in passing from one point in the volume to another.

Phase Diagram: The graphical representation of equilibrium states of existence of a system is known as phase diagram/constitution diagram.

The complexity of a phase diagram is primarily determined by a number of components which occur in the system, where components are chemical species of fixed composition.

Phase Diagram of One-component System:

It is a two dimensional representation of the dependence of the equilibrium state of existence of the two independent variables. Temperature & pressure are normally chosen as the two independent variables.

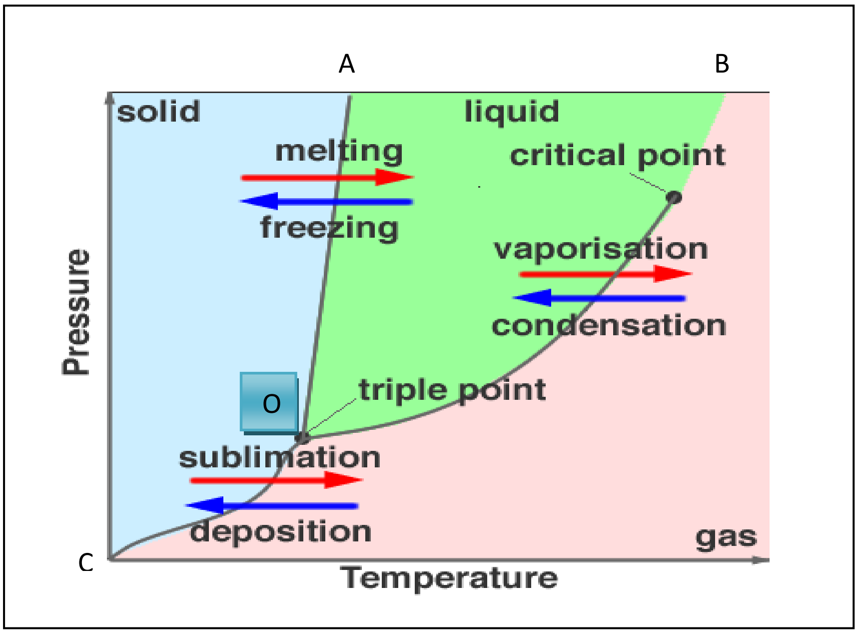

Fig 1.4: Schematic representation of part of phase diagram for H_2O

In the above figure 1.4 represents

Three areas AOC (solid), AOB (liquid), BOC (vapour) and all areas represents single phase. Any one out of this three phase areas of the phase diagram is said to be homogeneous system and if more than one phase then it is said to be heterogeneous system.

The lines OA – (Solid-Liquid) line, OB – (Liquid-Vapour) line, OC – (Solid-Vapour) line represents the simultaneously variations of P & T required for maintenance of equilibrium between two phase.

Point ‘O’ known as triple point where equilibrium lines meet which thus represents the unique values of P & T required for the establishment of three-phase equilibrium. It is central point that represents all the three phases i. e. solid, liquid, vapour.

1.9 GIBBS PHASE RULE:

- It is used to find out the number of independent variables associated with a system
- At invariant point degree of freedom is zero.
- Mathematically, Gibbs phase rule is given by

$$f = C - P + 2 \tag{1.4}$$

[Where

f – Degree of freedom
C – Number of components
P – Number of phases]

i. **Components:** It refers to the independent chemical species that constitute an alloy.
   Example: In Al-Cu system, there is two components involved as Al and Cu.
ii. **Degree of Freedom:** It refers to the number of independent variables associated with the system.

CHAPTER-2

FIRST LAW OF THERMODYNAMICS

2.1 FIRST LAW OF THERMODYNAMICS:

Let us consider a body in the state A, which performs work W, absorbs heat q & as a consequence moves to the state B. The absorption of heat increase the internal energy of the body by the amount ΔU & the performance of work W by the body decrease its internal energy by the amount W. Thus the total change in the internal energy of the body, ΔU is

$$\Delta U = (U_B - U_A) = q - W \tag{2.1}$$

This is the statement of **1st law of Thermodynamics.**

For an infinitesimal change of state the equation (1) can be written as in differential form as

$$dU = \delta q - \delta W \tag{2.2}$$

If the initial & final states are the same, then the integral of inexact differential may or may not be zero, but the integral of an exact differential is always zero.

$$\boxed{\begin{array}{c}\oint \delta W\ ,\oint \delta q = \text{May or may not zero.}\\ \oint dU = 0\end{array}} \longrightarrow \text{(Cyclic Process)}$$

$$\boxed{\begin{array}{l}\int_n^n \delta W, \int_n^n \delta q\ = \text{May or may not zero.}\\ \quad\int_n^n dU = 0\end{array}} \longrightarrow \text{(Processes where initial \& final states are same)}$$

First law defines in terms of equation (1) & (2), if we have considered that the process taking place in a closed system. In particular, if no work is done on a thermally isolated closed system. We have

$$\Delta U = 0$$

This is one aspect of the law of conservation of energy & can be stated as “The internal energy of an isolated system remains constant.”

First law also known as **conservation of energy**.

2.2 HEAT CAPACITY:

Heat capacity(C) is the quantity of heat required to raise the temperature of a substance by 1^0 C. Thus

$$C = \frac{q}{\Delta T} \tag{2.3}$$

If the temperature change is made vanishingly small, then

$$C = \frac{\delta q}{dT} \tag{2.4}$$

Heat capacity at constant volume

$$C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU+\delta W}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \tag{2.5}$$

Heat capacity at constant pressure

$$C_P = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{dU+PdV+VdP}{dT}\right)_P = \left(\frac{dH}{dT}\right)_V \tag{2.6}$$

2.2.1 Proof of $C_V = \left(\frac{dU}{dT}\right)_V$:

Since from first law of TD we know

$$\delta q = dU + \delta W = dU + PdV \tag{2.7}$$

At constant pressure U can be expressed in differential form as

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = f(V,T)_P \tag{2.8}$$

Put equation (2.8) in equation (2.7) we have

$$\delta q = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV \tag{2.9}$$

At constant volume equation (2.9) becomes

$$\delta q = \left(\frac{\partial U}{\partial T}\right)_V dT \Rightarrow \left(\frac{\delta q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.10}$$

Again at constant volume heat capacity can be expressed as

$$C_V = \left(\frac{\delta q}{dT}\right)_V \tag{2.11}$$

By considering above equation (2.10) and (2.11), we have got

$$C_V = \left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \tag{2.12}$$

2.2.2 Proof of $C_P = \left(\frac{dH}{dT}\right)_P$:

Since from first law of TD we know

$$\delta q = dU + \delta W = dU + PdV \tag{2.13}$$

At constant volume U can be expressed in differential form as

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT = f(P, T)_V \tag{2.14}$$

Put equation (2.14) in equation (2.13), we have got

$$\delta q = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT + PdV \tag{2.15}$$

At constant pressure equation (2.15) becomes

$$\delta q = \left(\frac{\partial U}{\partial T}\right)_P dT + PdV \tag{2.16}$$

$$\Rightarrow \left(\frac{\delta q}{dT}\right)_P = \left(\frac{dU + PdV}{dT}\right)_P dT = \left(\frac{dH}{dT}\right)_P \tag{2.17}$$

Again at constant pressure heat capacity can be expressed as

$$C_P = \left(\frac{\delta q}{dT}\right)_P \tag{2.18}$$

By considering above equation (2.17) and (2.18), we have got

$$C_P = \left(\frac{\delta q}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P \tag{2.19}$$

2.2.3 Relation Between C_P & C_V:

Since from first law of TD we know

$$\delta q = dU + \delta W = dU + PdV \tag{2.20}$$

At constant pressure U can be expressed in differential form as

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{2.21}$$

Put equation (2.21) in equation (2.20) we have

$$\delta q = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV \tag{2.22}$$

Taking derivative of equation (2.22) w.r.t. T, we got

$$\frac{\delta q}{dT} = \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + \left(\frac{\partial U}{\partial T}\right)_V + \frac{PdV}{dT} \tag{2.23}$$

At constant pressure equation (2.23) becomes

$$\left(\frac{\delta q}{dT}\right)_P = C_P = \left(\frac{dU}{dV}\right)_T \frac{dV}{dT} + C_V + \frac{PdV}{dT} \tag{2.24}$$

$$\Rightarrow C_P - C_V = \left(\frac{dU}{dV}\right)_T \frac{dV}{dT} + \frac{PdV}{dT} \tag{2.25}$$

For ideal gas derivative of U w.r.t. V is zero. So equation (2.25) becomes

$$C_P - C_V = \frac{PdV}{dT} = R \tag{2.26}$$

2.3 ENTHALPY:

It is a defined thermodynamics potential designated by the letter “H”, that consists of the internal energy (U) of the system plus the product of the pressure (P) & volume (V) of the system. Mathematically it is given by

$$H = U + PV \tag{2.27}$$

At constant pressure process

$$\int_{H_1}^{H_2} \Delta H = H_2 - H_1 = (\Delta q)_P = \int_{U_1}^{U_2} \Delta U + P\int_{V_1}^{V_2} \Delta V \tag{2.28}$$

$$\Rightarrow H_2 - H_1 = (\Delta q)_P = (U_2 - U_1) + P(V_2 - V_1) \tag{2.29}$$

At constant volume process

$$\int_{H_1}^{H_2} \Delta H = H_2 - H_1 = (\Delta q)_V = \int_{U_1}^{U_2} \Delta U \tag{2.30}$$

(Since at constant volume work done PdV becomes zero)

$$\Rightarrow H_2 - H_1 = U_2 - U_1 \tag{2.31}$$

2.4 HESS’S LAW:

The law states that ”The total change of heat in a chemical reaction is same irrespective whether it occurs in a single step or in multiple steps provided that the reaction must be isothermal or isobaric or isochoric.”

If a process occur from A to B, then using Hess's law we can write as enthalpy change throughout the path AB is equal to sum of the enthalpies throughout AC, CD and DA.

$$\begin{tikzcd} A \arrow[r] \arrow[d] & B \\ C \arrow[r] & D \arrow[u] \end{tikzcd}$$

$$\mathrm{H_{AB}} = \Delta\mathrm{H_{AC}} + \Delta\mathrm{H_{CD}} + \Delta\mathrm{H_{DA}} \tag{2.32}$$

Problem-2.1: Calculate the heat of the reaction for the formation of solid WO_3 from solid W and O_2 gas i.e.

Reaction 2.1: $\langle W\rangle + \frac{3}{2}(O_2) = \langle WO_3\rangle$ at 298 K.

Given the following data at 298 K and 1 atm pressure:

Reaction 2.2: $\langle W\rangle + (O_2) = \langle WO_2\rangle\,;\ \Delta H^0_{298} = -134\ kcal$

Reaction 2.3: $3\langle WO_2\rangle + (O_2) = \langle W_3O_8\rangle\,;\ \Delta H^0_{298} = -131.5\ \ kcal$

Reaction 2.4: $\langle W_3O_8\rangle + \frac{1}{2}(O_2) = 3\langle WO_3\rangle\,;\ \Delta H^0_{298} = -66.5\ \ kcal$

Solution: The problem consists of calculation of standard heat of the following reaction (2.1) at 373 K & 1 atm pressure where standard heat of the reaction (2.2), (2.3), (2.4) are given

Reaction 2.1: $\langle \mathrm{W}\rangle + \frac{3}{2}(\mathrm{O_2}) = \langle \mathrm{WO_3}\rangle\,;\ \Delta\mathrm{H}^0_1$

Reaction 2.2: $\langle \mathrm{W}\rangle + (\mathrm{O_2}) = \langle \mathrm{WO_2}\rangle\,;\ \Delta\mathrm{H}^0_2 = \Delta\mathrm{H}^0_{298} = -134\ \mathrm{kcal}$

Reaction2.3: $3\langle \mathrm{WO_2}\rangle + (\mathrm{O_2}) = \langle \mathrm{W_3O_8}\rangle\,;\ \Delta\mathrm{H}^0_3 = \Delta\mathrm{H}^0_{298} = -131.5\ \ \mathrm{kcal}$

Reaction 2.4: $\langle \mathrm{W_3O_8}\rangle + \frac{1}{2}(\mathrm{O_2}) = 3\langle \mathrm{WO_3}\rangle\,;\ \Delta\mathrm{H}^0_4 = \Delta\mathrm{H}^0_{298} = -66.5\ \ \mathrm{kcal}$

Let us consider at standard state, heat of reaction of reaction (2.1), (2.2), (2.3) & (2.4) are$\Delta\mathrm{H}^0_1$,$\Delta\mathrm{H}^0_2$, $\Delta\mathrm{H}^0_3$ & $\Delta\mathrm{H}^0_4$ respectively. Then standard heat of reaction at 298 K can be calculated as

$$\Delta\mathrm{H}^0_1 = \Delta\mathrm{H}^0_2 + \frac{\Delta\mathrm{H}^0_3}{3} + \frac{\Delta\mathrm{H}^0_4}{3} = -200\ \mathrm{K\,Cal.}$$

2.5 KIRCHHOFF'S LAW:

Kirchhoff's law states that "If a system undergoes a change from one state to another state then both internal energy & heat occur would alter."

Mathematically Kirchhoff's law can be expressed as

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta C_P)_{\text{Reaction}}\, dT \qquad (2.33)$$

$$\Rightarrow \left[\Delta H_{T_2} - \Delta H_{T_1}\right] = \int_{T_1}^{T_2} [(\sum C_P)_{\text{Product}} - (\sum C_P)_{\text{Reactant}}]\, dT \qquad (2.34)$$

$$\Rightarrow \left[\Delta H_{T_2}\right] = \left[\Delta H_{T_1}\right] + \int_{T_1}^{T_2} [(\sum C_P)_{\text{Product}} - (\sum C_P)_{\text{Reactant}}]\, dT$$

(2.35)

2.6 THERMO CHEMISTRY & ITS APPLICATIONS:

It is the study of heat effects accompanying chemical reactions, the formation of solutions & changes in the state of matter such as melting or vaporization & physic-chemical processes.

2.6.1 Heat of Reaction: It is defined as the heat evolved or absorbed when the reactants react completely to produce products.

- Expressed in terms of either per mole of any reactant or any products.

2.6.2 Heat of Formation: It is defined as the heat evolved or absorbed when one mole of the compound is formed from its constituent elements.

- Expressed per mole of compound.
- Depends on temperature.
- In standard state, heat of formation of a compound out of its constituent elements is called as standard heat of formation.

2.6.3 Heat of Combustion: Heat of combustion of a substance is the enthalpy change when one mole of the substance is completely burnt in oxygen.

2.6.4 Heat of Solution: When one substance dissolves in another there will be a change in enthalpy that is known as heat of solution & it depends on the concentration of the solution.

N.B.: General expression of C_p is

$$C_P = aT + bT^2 + cT^{-1} + d \qquad (2.36)$$

Problem-2.2: Calculate the standard heat of formation of PbO from Pb & O_2 at 227^0C from the following data:

$\Delta H^0_{298, <PbO>}$ = -52.4 Kcal/mol, $C_{P, <PbO>} = 10.6 + 4.0x10^{-3}T$ Cal/deg/mol

$C_{p, <Pb>} = 5.63+2.33x10^{-3}T$ Cal/deg/mol, $C_{p, (O2)} = 7.16+1.0x10^{-3}T-0.4x10^5T^{-2}$ Cal/deg/mol

Solution:

For the reaction

Reaction 2.5: $\langle \mathrm{Pb}\rangle + \frac{1}{2}(\mathrm{O_2}) = \langle \mathrm{PbO}\rangle$

We can calculate the standard heat of formation of PbO by using the equation mentioned below

$$\Delta \mathrm{H}^0_{500\ \mathrm{K},<PbO>} = \Delta \mathrm{H}^0_{298,<PbO>} + \int_{298}^{500} (\Delta \mathrm{C_p})_{\mathrm{Rea(1)}}\, \mathrm{dT}$$

$$= \Delta \mathrm{H}^0_{298,<PbO>} + \int_{298}^{500} \left[(\mathrm{C_p})_{<PbO>} - (\mathrm{C_p})_{<Pb>} - \frac{1}{2}(\mathrm{C_p})_{(\mathrm{O_2})}\right] \mathrm{dT}$$

$$\Rightarrow \Delta \mathrm{H}^0_{500,<PbO>} = -51{,}998\ \mathrm{cal}$$

2.7 ADIABATIC & ISOTHERMAL PROCESS:

2.7.1 Adiabatic Process:

It states that the heat change in the system is zero i. e. no heat enters or leaves the system.

In Adiabatic system, it obey the following equations

$$\mathrm{P_1 V_1^\gamma = P_2 V_2^\gamma} \tag{2.37}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \tag{2.38}$$

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma \tag{2.39}$$

Work done in reversible adiabatic process given by

$$\Delta W = \frac{P_2V_2 - P_1V_1}{1-\gamma} = C_V(T_2 - T_1) \tag{2.40}$$

2.7.2 Isothermal Process: It states that the net temperature change throughout the process is zero i.e. $\Delta T = 0$.

Reversible Isothermal Process: When an ideal gas of mass m undergoes a reversible process from state 1 to state 2, and then work done is given by

$$\int_1^2 \delta W = \int_{V_1}^{V_2} P dV \tag{2.41}$$

$$\Rightarrow W_{1-2} = W_1 - W_2 = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{mRT}{V} dV \tag{2.42}$$

(Since PV = mRT)

$$\Rightarrow W_{1-2} = mRT \ \ln\left({V_2}/{V_1} \right) = mRT \ln\left({P_1}/{P_2} \right) \tag{2.43}$$

The heat transfer involved in the process

$$q_{1-2} = mRT \ln\left({V_2}/{V_1} \right) = T(S_2 - S_1) \tag{2.44}$$

CHAPTER-3

SECOND LAW OF THERMODYNAMICS

3.1 SECOND LAW OF THERMODYNAMICS:

The 2nd law of TD has been stated in several equivalent forms such as implicitly by Carnot (1824) & explicitly first by Clausius (1950) & later on independently by Kelvin (1951). According to Clausius & Kelvin & as reformulated by Max Plank, the following statement is significant:

"It is impossible to construct a cyclic engine that can convert heat from a reservoir at a uniform temperature completely into mechanical energy without leaving any effect elsewhere."

The engine must be cyclic i.e. it returns to initial position after each stroke or revolution.

3.1.1 Some Alternative Statements:

i. Heat absorbed at any one temperature can not completely transformed into work without leaving some change in the system or its surrounding.

ii. Spontaneous processes are not thermodynamically reversible.

3.1.2 Spontaneous Process:

Spontaneous processes are the naturally occurring processes which cannot be reversed without the interruption of external force.

Examples of Spontaneous processes: Flow of heat from higher to lower temperature, diffusion process of a species from higher to lower concentration, mixing of acid-base reactions, all natural processes that occurring in nature without external intervention.

Generally 2nd law of TD mathematically expressed in terms of entropy(S) as

$$dS = \frac{\delta q_{rev}}{T} \tag{3.1}$$

3.2 ENTROPY:

Entropy is a measure of randomness of a system. Entropy increases as the number of possible microstates increases where microstate is the microscopic arrangement of atoms or particles.

- Symbolically represented as by “S”.
- Standard Entropy (S^0): The absolute entropy of a substance at 1atm pressure and 298 K temperature.
- Unit: J/K.mol.
- Trends for standard entropy values
  a. Entropy of solid < Liquid < Gas
  b. More complexes molecules have higher entropy.

3.2.1 Characteristics of Entropy:

i. It depends on state variables.
ii. It is a perfect differential since it is a state property.
iii. It is mathematically expressed as$dS = \frac{\delta q_{rev}}{T}$.
iv. For absorption of heat δq is positive. So entropy change dS is positive. Similarly for release of heat δq is negative. So entropy change dS is negative.
v. For adiabatic process, δq is equal to zero. Hence dS is equal to zero. So adiabatic process also known as isotropic process.

3.2.2 Proof of δq is not Perfectly Differentiable, but $\left(\delta q/_T\right)$ is Perfectly Differentiable:

Since, from 1st law of Thermodynamics, we know

$$\delta q = dU + \delta W \tag{3.2}$$

Again, we know $dU = C_V dT$ & $\delta W = PdV$. So equation (3.2) becomes

$$\delta q = C_V dT + PdV = C_V dT + RT\frac{dV}{V} \tag{3.3}$$

(Since molar quantity we have $P = \frac{RT}{V}$)

Now consider the process undergo from state-1 to state-2, we have equation (3.3) becomes

$$\int_1^2 \delta q = \int_{T_1}^{T_2} C_V\, dT + \int_{V_1}^{V_2} RT\frac{dV}{V} = C_V(T_2 - T_1) + RT(\ln V_2 - \ln V_1) \tag{3.4}$$

$$\Rightarrow \int_1^2 \delta q = \underset{\substack{\Downarrow\\ \boxed{1^{st}\text{ Term}}}}{C_V\Delta T} + \underset{\substack{\Downarrow\\ \boxed{2^{nd}\text{ Term}}}}{RT\ln(\frac{V_2}{V_1})} \tag{3.5}$$

In above equation, we have

i. For isothermal process, 1st term is zero. So δq depends on 2nd term.
ii. For non-isothermal process, both terms are not completely zero. So δq depends on both terms.

Since δq not depends on state variables. So it is not a perfectly differentiable.

Again,

$$\int_1^2 \frac{\delta q}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R \frac{dV}{V} \tag{3.6}$$

(Dividing equation (3.3) by T)

$$\Rightarrow \int_1^2 \frac{\delta q}{T} = C_V(\ln T_2 - \ln T_1) + R(\ln V_2 - \ln V_1) \tag{3.7}$$

$$\Rightarrow \int_1^2 \frac{\delta q}{T} = \underbrace{C_V \ln\left(\frac{T_2}{T_1}\right)}_{1^{st}\text{ Term}} + \underbrace{R \ln\left(\frac{V_2}{V_1}\right)}_{2^{nd}\text{ Term}} \tag{3.8}$$

Since, $\frac{\delta q}{T}$ depends on at least one state varies when others remains constant.

i. For Isothermal process, $\frac{\delta q}{T}$ depends on 2nd term.
ii. For Isochoric process, $\frac{\delta q}{T}$ depends on 1st term.

So, $\frac{\delta q}{T}$ is perfectly differentiable.

3.3 ENTROPY OF A PERFECT GAS:

Dividing equation of 1st law by temperature (T), we have

$$\int_1^2 \frac{\delta q}{T} = \int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R \frac{dV}{V} \tag{3.9}$$

$$\Rightarrow \Delta S = S_2 - S_1 = C_V(\ln T_2 - \ln T_1) + R(\ln V_2 - \ln V_1) = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) \tag{3.10}$$

$$\Rightarrow S_2 = C_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) + S_1 \tag{3.11}$$

Now we know,

$$\left.\begin{aligned} & C_P - C_V = R \Rightarrow C_V = C_P - R \\ \& \quad & V = \frac{RT}{P} \end{aligned}\right\} \tag{3.12}$$

So using equation (3.12) in equation (3.11), it will become

$$S_2 = (C_p - R)\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{RT_2/P_2}{RT_1/P_1}\right) + S_1$$

$$= C_P\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{T_2}{T_1}\right) + R\ln\left[\left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right)\right] + S_1 \quad (3.13)$$

$$\Rightarrow S_2 = C_P\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{P_1}{P_2}\right) + S_1$$

$$= C_P\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right) + S_1 \quad (3.14)$$

In general the above equation (3.14) can be represented as

$$S = C_P\ln T - R\ln P + S_o \quad (3.15)$$

Now putting $T = \frac{PV}{R}$ in above equation (3.15) we have

$$S = C_P\ln\left(\frac{PV}{R}\right) - R\ln P + S_o = C_P\ln P + C_P\ln V - C_P\ln R - R\ln P + S_o \quad (3.16)$$

(Since $C_P\ln R$ is a constant. So adding with S_o another constant get obtained S_I)

$$\Rightarrow S = C_P\ln P + C_P\ln V - R\ln P + S_I = (C_P - R)\ln P + C_P\ln V + S_I$$

$$\Rightarrow S = C_V\ln P + C_P\ln V + S_I \quad (3.17)$$

So for a process which undergoes from state (1) to state (2) equation (3.17) can be expressed as

$$\Delta S = S_2 - S_1 = C_V\ln\left(\frac{P_2}{P_1}\right) + C_P\ln\left(\frac{V_2}{V_1}\right) \quad (3.18)$$

At Isothermal condition (ΔT=0), equation (3.11) and (3.14) becomes

$$S_2 = R\ln\left(\frac{V_2}{V_1}\right) + S_1 \quad (3.19)$$

$$S_2 = -R\ln\left(\frac{P_2}{P_1}\right) + S_1 \quad (3.20)$$

From equation (3.19) & (3.20), we have got

$$\Delta S = S_2 - S_1 = R\ln\left(\frac{V_2}{V_1}\right) = -R\ln\left(\frac{P_2}{P_1}\right) \quad (3.21)$$

3.4 TEMPERATURE DEPENDENCE OF ENTROPY:

We know

$$H = U + PV \quad (3.22)$$

$$\Rightarrow dH = d(U + PV) = dU + PdV + VdP = \delta q + VdP \quad (3.23)$$

Now putting $\delta q = TdS$ & $dH = C_P dT$ in equation (3.23) we have

$$C_P dT = TdS + VdP \tag{3.24}$$

Now dividing the equation (3.24) by T we have

$$C_P\left(\frac{dT}{T}\right) = dS + \frac{VdP}{T} \tag{3.25}$$

At constant pressure the above equation becomes

$$C_P\left(\frac{dT}{T}\right) = dS \tag{3.26}$$

Integrating equation (2.26) from state 1 to state 2, we have got

$$\int_1^2 dS = C_P \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Rightarrow \Delta S = S_2 - S_1 = C_P(\ln T_2 - \ln T_1)$$

$$\Rightarrow \Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) \tag{3.27}$$

Again, we know

$$\delta q = dU + PdV = C_V dT + PdV \tag{3.28}$$

Dividing equation (2.28) by T at constant volume, equation (2.28) becomes

$$\frac{\delta q}{T} = C_V \frac{dT}{T} \Rightarrow dS = C_V \frac{dT}{T} \tag{3.29}$$

Integrating equation (2.29) from state-1 to state-2, we got

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Rightarrow \Delta S = S_2 - S_1 = C_V \ln\left(\frac{T_2}{T_1}\right) \tag{3.30}$$

3.5 REVERSIBLE & IRREVERSIBLE PROCESS:

Sl no.	Reversible Process	Irreversible Process
1	It is defined as the hypothetical passage of a system through a series of equilibrium stages.	The process that can't be reversed or changed back (permanent damage).
2	Very slow & mostly impractible in nature.	Generally at normal condition it occurs. It may be very fast or fast or slow & practically possible.
3	For isolated system $dS_{sys} = 0$	For isolated system $dS_{sys} > 0$

CHAPTER-4

AUXILIARY FUNCTIONS & RELATIONS, CRITERIA FOR EQUILIBRIA

4.1 FREE ENERGY:

Free energy is defined as the part of energy that available for useful work done & that part of energy which can not available for useful work done is known as bound energy.

- Total energy (E) is the sum of free energy (A) and bound energy (B).
- The following two functions are employed in TD, according to the names of the scientists who proposed them.

$$\text{Helmholtz free energy } (A) = U - TS \qquad (4.1)$$

$$\text{Gibbs free energy } (G) = H - TS \qquad (4.2)$$

- Since U, S, H etc. are the state properties & T is also a state variable. So F and G are also state properties.
- Below Table is showing, how the nature of the reaction depends on sign of ΔH, ΔS & ΔG.

ΔH	ΔS	ΔG	**Reaction Outcome**
Negative	Positive	Always Negative	Reaction is Spontaneous at all Temperature.
Positive	Negative	Always Positive	Reaction is Non-spontaneous in all Temperature
Negative	Negative	Negative at low Temperature	Reaction is Spontaneous at low Temperature.
		Positive at high Temperature	Reaction is Non-spontaneous in high Temperature
Positive	Positive	Positive at low Temperature	Reaction is Non-spontaneous in low Temperature.
		Negative at low Temperature	Reaction is Spontaneous at high Temperature

4.2 COMBINED EXPRESSIONS OF 1^{ST} & 2^{ND} LAW OF THERMODYNAMICS:

Assumptions:

- Closed System
- Reversible Process
- Work done against pressure

From 1st law of Thermodynamics, we know that

$$dU = \delta q - \delta W = \delta q - PdV \tag{4.3}$$

From 2nd law of Thermodynamics, we know that

$$\delta q = TdS \tag{4.4}$$

Combining equation (4.3) and (4.4), we got

$$dU = TdS - PdV \tag{4.5}$$

Again, we know

$$dH = dU + PdV + VdP \tag{4.6}$$

Replacing the term dUfrom the equation (4.5) in the equation (4.6), it will become

$$dH = (TdS - PdV) + PdV + VdP = TdS + VdP \tag{4.7}$$

From Helmholtz free energy equation, we know

$$A = U - TS \Rightarrow dA = dU - (TdS + SdT) = (TdS - PdV) - (TdS + SdT) \tag{4.8}$$

$$\Rightarrow dA = TdS - PdV - TdS - SdT = -PdV - SdT \tag{4.9}$$

From Gibbs free energy equation, we know

$$G = H - TS \Rightarrow dG = dH - (TdS + SdT) = (TdS + VdP) - (TdS + SdT) \tag{4.10}$$

$$\Rightarrow dG = TdS + VdP - TdS - SdT = VdP - SdT \tag{4.11}$$

So, combining 1st & 2nd laws of Thermodynamics with considering the assumptions. We got the following equations

$$dU = TdS - PdV \tag{4.12}$$

$$dH = TdS + VdP \tag{4.13}$$

$$dA = -PdV - SdT \tag{4.14}$$

$$dG = VdP - SdT \tag{4.15}$$

The above four basic differential equations (4.12-4.15) are valid under above assumptions i.e. for closed and isolated systems which have fixed mass and composition. The equations are also applicable for open systems provided under a fixed mass and composition.

4.3 CRITERIA OF THERMODYNAMICS EQUILIBRIA:

Simply it is known as criteria of equilibrium. At equilibrium, there is no change in the system i.e. system remains stable. Again the reversible process occurs through a series of equilibrium stages. Therefore, we keep the independent variables should be fixed to obtained equilibrium criteria. So, in the previous four basic equations to get equilibrium criteria we should have keep the right hand side independent variables as constant.

Equilibrium Criteria

Basic Equations	**Differential Form**	**Finite Difference Form**
$dU = TdS - PdV$	$(dU)_{S,V} = 0$	$(\Delta U)_{S,V} = 0$
$dH = TdS + VdP$	$(dH)_{S,P} = 0$	$(\Delta H)_{S,P} = 0$
$dA = -SdT - PdV$	$(dA)_{T,V} = 0$	$(\Delta A)_{T,V} = 0$
$dG = -SdT + VdP$	$(dG)_{T,P} = 0$	$(\Delta G)_{T,P} = 0$

N.B.: Since it is easy to maintain the temperature & pressure constant. So Gibbs free energy criterion achieved which get employ in Chemical & Metallurgical thermodynamics.

4.4 GIBBS HELMHOLTZ EQUATION:

From Helmholtz free energy equation, we have

$$dA = -PdV - SdT \tag{4.16}$$

From Gibbs free energy equation, we have

$$dG = VdP - SdT \tag{4.17}$$

4.4.1 Isochoric Process:

$$dA = -SdT \Rightarrow \left(\frac{dA}{dT}\right)_V = -S \tag{4.18}$$

Then as, $A = U - TS \Rightarrow -S = \frac{A-U}{T}$ (4.19)

From equation (4.16) and (4.17), we have

$$\left(\frac{dA}{dT}\right)_V = \frac{A-U}{T} \Rightarrow A - U = T\left(\frac{dF}{dT}\right)_V \tag{4.20}$$

$$\Rightarrow A = U + T\left(\frac{dF}{dT}\right)_V \tag{4.21}$$

4.4.2 <u>For Isobaric Process:</u>

$$dG = -SdT \Rightarrow \left(\frac{dG}{dT}\right)_P = -S \tag{4.22}$$

Again we know, $G = H - TS \Rightarrow -S = \frac{G-H}{T}$ (4.23)

From equation (4.20) and (4.21), we got

$$\left(\frac{dG}{dT}\right)_P = \frac{G-H}{T} \Rightarrow G - H = T\left(\frac{dG}{dT}\right)_P \tag{4.24}$$

$$\Rightarrow G = H + T\left(\frac{dG}{dT}\right)_P \tag{4.25}$$

The above equations (4.19) and (4.23) are known as Gibbs Helmholtz equation.

4.5 <u>MAXWELL'S RELATION:</u>

Since considering the combination of 1st and 2nd law of Thermodynamics, we got the equations (4.12-4.15)

4.5.1 <u>Take equation (4.12):</u>

(a) At constant entropy:

$$\partial U = -P\,\partial V \Rightarrow \left(\frac{\partial U}{\partial V}\right)_S = -P \tag{4.26}$$

$$\Rightarrow \frac{\partial^2 U}{\partial S\ \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4.27}$$

(b) At constant volume:

$$\partial U = T\,\partial S \Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \tag{4.28}$$

$$\Rightarrow \frac{\partial^2 U}{\partial S\ \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \tag{4.29}$$

From equation (4.27) and (4.29), we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4.30}$$

4.5.2 <u>Take equation (4.13):</u>

(a) At constant entropy:

$$\partial \mathrm{H} = \mathrm{V}\,\partial \mathrm{P} \Rightarrow \left(\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{S}} = \mathrm{V} \tag{4.31}$$

$$\Rightarrow \frac{\partial^2 \mathrm{H}}{\partial \mathrm{S}\ \partial \mathrm{P}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{P}} \tag{4.32}$$

(b) At constant pressure:

$$\partial \mathrm{H} = \mathrm{T}\,\partial \mathrm{S} \Rightarrow \left(\frac{\partial \mathrm{H}}{\partial \mathrm{S}}\right)_{\mathrm{P}} = \mathrm{T} \tag{4.33}$$

$$\Rightarrow \frac{\partial^2 \mathrm{H}}{\partial \mathrm{S}\ \partial \mathrm{P}} = \left(\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{S}} \tag{4.34}$$

From equation (4.32) and 4.34), we got

$$\left(\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{S}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{P}} \tag{4.35}$$

4.5.3 <u>Take equation (4.14):</u>

(a) At constant temperature:

$$\partial \mathrm{A} = -\mathrm{P}\,\partial \mathrm{V} \Rightarrow \left(\frac{\partial \mathrm{A}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = -\mathrm{P} \tag{4.36}$$

$$\Rightarrow \frac{\partial^2 \mathrm{A}}{\partial \mathrm{V}\ \partial \mathrm{T}} = -\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

(4.37)

(b) At constant volume:

$$\partial \mathrm{A} = -\mathrm{S}\,\partial \mathrm{T} \Rightarrow \left(\frac{\partial \mathrm{A}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = -\mathrm{S} \tag{4.38}$$

$$\Rightarrow \frac{\partial^2 \mathrm{A}}{\partial \mathrm{T}\ \partial \mathrm{V}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \tag{4.39}$$

From equation (4.37) and (4.39), we got

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \tag{4.40}$$

4.5.4 <u>Take equation (4.15):</u>

(a) At constant pressure:

$$\partial \mathrm{G} = -\mathrm{S}\,\partial \mathrm{T} \Rightarrow \left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -\mathrm{S} \tag{4.41}$$

$$\Rightarrow \frac{\partial^2 \mathrm{G}}{\partial \mathrm{P}\ \partial \mathrm{T}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{T}} \tag{4.42}$$

(b) At constant temperature:

$$\partial \mathrm{G} = \mathrm{V}\,\partial \mathrm{P} \Rightarrow \left(\frac{\partial \mathrm{G}}{\partial \mathrm{P}}\right)_{\mathrm{T}} = \mathrm{V} \qquad (4.43)$$

$$\Rightarrow \frac{\partial^2 \mathrm{G}}{\partial \mathrm{T}\ \partial \mathrm{P}} = \left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} \qquad (4.44)$$

From equation (4.42) and (4.44), we got

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -\left(\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{T}} \qquad (4.45)$$

So the above equations (4.30), (4.35), (4.40) and (4.45) are known as **Maxwell's relations**.

4.6 TRANSFORMATION FORMULA:

For state property x, y, z. The system X represented as

$$\mathrm{X} = \mathrm{f}(\mathrm{x},\mathrm{y},\mathrm{z}) = \left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} \mathrm{dy} + \left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}} \mathrm{dz} \qquad (4.46)$$

So for increase in change at constant composition X=0, so equation (4.44) becomes

$$0 = \left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} \mathrm{dy} + \left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}} \mathrm{dz}$$

$$\Rightarrow \left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} \mathrm{dy} = -\left(\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}} \mathrm{dz}$$

$$\Rightarrow \left(\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} \left(\frac{\partial \mathrm{y}}{\partial \mathrm{z}}\right)_{\mathrm{x}} \left(\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}} = -1 \qquad (4.47)$$

The above equation (4.47) is known as Transformation formula.

CHAPTER-5

THIRD LAW OF THERMODYNAMICS, STATISTICAL THERMODYNAMICS

5.1 THIRD LAW OF THERMODYNAMICS:

In 1906, W. Nernst proposed his heat theory on the basis of experimental evidence. It was later generalized by Max Plank as "The entropy of any substance (which is at complete equilibrium) may take as Zero at 0K." This is known as Third law of Thermodynamics.

5.1.1 Consequences of 3rd Law of Thermodynamics:

When disorder in a substance completely vanishes, it becomes perfectly ordered and has only one possible arrangement of atoms. Then and only then a complete internal equilibrium is established. The causes for deviation from perfect order are

i. Thermal energy and resulting motion of atoms and molecules (at T = 0K).
ii. Non-crystallinity, as in amorphous solids and liquids.
iii. Crystal defects-vacancies, interstitial atoms, dislocation.
iv. Disordered compound structure.
v. Disordered solid solution.

At T = 0K, thermal energy is zero. Thus this source of disorder gets eliminated. But other sources remain there. In reality it is difficult to achieve exactly zero entropy at T = 0K.

Actually, all disorders are caused by thermal energy which get lowered continuously and vanish at T = 0K provided internal equilibrium exists.

5.2 STATISTICAL THERMODYNAMICS:

It is originated from kinetic Theory of gases, which related to average kinetic energy of molecules in an ideal gas. The application of probability theory, quantum theory and statistical mechanics allowed it to arrive at microscopic thermodynamics relations from atomistic (i. e. microscopic) point of view. It was founded by Maxwell, Gibbs and Boltzmann in 19th century and it was developed further in the 1920 and 1930.

5.2.1 Micro-State of a system:

Consider a system consisting of gas where particles are in a constant state of motion which may be translational, rotational or vibrational.

Due to these motions particles inside the system occupy different positions in different instant of time. On the other hand due to collision among themselves and wall of the container, velocities change with time. Thus particles inside a system has six different coordinates as (x, y, z) and three are velocity co-ordinates as (V_X, V_Y, V_Z).

If at any instant of time all these six co-ordinates are well-defined for each particle present inside the system then such a complete specification define a micro-state of a system.

5.2.2 Ensamble:

An Ensamble of a system can be defined by a set which consists of all the possible micro-state of a system. This is because with the passage of time a system passes from one micro-state to other as a result of which individual particles within the system attains different set of position as well as velocity co-ordinates.

N.B.:

Micro-Cannonical Ensamble: Micro-state of an isolated system having constant volume is called micro-Cannonical Ensamble.

5.2.3 Macro-state of a System:

The different macro-state of Ensamble can be arranged into a no. of subset in a way that any one of the subset consists of such micro-state which have same number of particles lying between the co-ordinates $(\mathrm{X}, \mathrm{Y}, \mathrm{Z}, \mathrm{V_X}, \mathrm{V_Y}, \mathrm{V_Z})$ and $(\mathrm{X} + \delta\mathrm{X}, \mathrm{Y} + \delta\mathrm{Y}, \mathrm{Z} + \delta\mathrm{Z}, \mathrm{V_X} + \delta\mathrm{V_X}, \mathrm{V_Y} + \delta\mathrm{V_Y}, \mathrm{V_Z} + \delta\mathrm{V_Z}$). Thus subsets are called macro-state of a system.

5.3 POSTULATES OF STATISTICAL THERMODYNAMICS:

5.3.1 First Postulate: It stated as "The time average of a mechanical variable such as average energy of a system is equal to the Ensamble average representing the Ensamble, provided the number of microstate representing the system are infinitely large. "

Derivation: Let the isolated system consists of n number of particles out of which n_1 particles having energy U_1. Similarly n_2 particles having U_2 ... up to n_i particles having U_i. Hence the total energy U which is constant for the system can be expressed as

$$U = U_1 n_1 + U_2 n_2 + \cdots + U_i n_i = \sum U_i n_i \tag{5.1}$$

As the total number of particles in the system is also constant i.e. n

$$\mathrm{n} = \mathrm{n_1} + \mathrm{n_2} + \cdots + \mathrm{n_i} = \sum_{\mathrm{i}=1}^{\mathrm{i}} \mathrm{n_i} \tag{5.2}$$

If ω be the number of microstate present in a macrostate

$$w = \frac{n!}{n_1!\, n_2! \ldots\ldots n_i!} = \frac{n!}{\prod_i n_i!} \tag{5.3}$$

5.3.2 **Second Postulates:** It is stated as "All microstate are equally probable therefore the probability of a system to represent in a particular microstate is directly proportional to the number of microstate present in the macrostate."

Hence macrostate of higher number of microstate well define the macroscopic properties of the system.

5.3.3 Maxwell-Boltzmann Statistics:

It stated as "Particles in a microstate are distinguished from each other on the basis of the total energy content by each particle."

Limitation: If there is an isolated system of constant volume then two or more particles have same energy level. Then it is difficult to distinguish the particles from each other. This problem gets solved under Boltzmann- Einstein statistics.

5.3.4 Boltzmann-Einstein Statistics:

It stated as "Particles of same energy and size get distinguished from each other on the basis of orientation or degeneracy principle."

Suppose there are n_i number of particles with energy U_I in which there are g_i states of energy (degenerate state energy). To place n_i particles in g_i sections we need (g_i+1) partitions.

Let us assume without any restriction n_i particles are allowed to move in g_i sections. So the n_i particles arranged among themselves and that (g_i+1) partitions are among themselves in $n_i!$ and $(g_i-1)!$ Ways respectively. Then the particles and partitions internally arranged among themselves in $(n_i+g_i-1)!$ Ways. So the number in which n_i particles get allocated in g_i state of degeneracy can be expressed as

$$\text{Total possible no. of degenration to accomodate } n_i \text{ particles} = \left(\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}\right) \tag{5.4}$$

Number of microstates in a macrostate of an isolated system of constant volume

$$= \left(\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}\right) \tag{5.5}$$

5.4 STALIN FORMULA:

It is used to find out the probability of total number of microstates.

Since we know

$$\ln x! = x\ln x - x \tag{5.6}$$

So we have

$$\ln w = \ln\left[\frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}\right] = \ln(n_i+g_i-1)! - \ln n_i! - \ln(g_i-1)! \tag{5.7}$$

Now neglecting the unity terms in comparison to the highest energy level, the equation (5.7) becomes

$$\ln w = \ln\left[\frac{(n_i+g_i)!}{n_i!g_i!}\right] = \ln(n_i+g_i)! - \ln n_i! - \ln g_i! \tag{5.8}$$

$$\Rightarrow \ln w = \sum[(n_i+g_i).\ln(n_i+g_i) - (n_i+g_i) - (n_i\ln n_i - n_i) - (g_i\ln g_i - g_i)] \tag{5.9}$$

$$\Rightarrow \ln w = \sum[(n_i+g_i).\ln(n_i+g_i) - n_i - g_i - n_i\ln n_i + n_i - g_i\ln g_i + g_i] \tag{5.10}$$

$$\Rightarrow \ln w = \sum[n_i\ln(n_i+g_i) + g_i\ln(n_i+g_i) - n_i\ln n_i - g_i\ln g_i] \tag{5.11}$$

$$\Rightarrow \ln w = \sum[n_i(\ln(n_i+g_i) - \ln n_i) + g_i(\ln(n_i+g_i) - \ln g_i)] \tag{5.12}$$

$$\Rightarrow \ln w = \sum[n_i(\ln(n_i+g_i) - \ln n_i) + g_i(\ln(n_i+g_i) - \ln g_i)] \tag{5.13}$$

$$\Rightarrow \ln w = \sum\left[n_i\ln\left(\frac{n_i+g_i}{n_i}\right) + g_i\ln\left(\frac{n_i+g_i}{g_i}\right)\right] \tag{5.14}$$

$$\Rightarrow \ln w = \sum\left[n_i\ln\left(1+\frac{g_i}{n_i}\right) + g_i\ln\left(1+\frac{n_i}{g_i}\right)\right] \tag{5.15}$$

5.5 RELATIONSHIP BETWEEN STATISTICAL INTERPRETATIONS OF ENTROPY:

Entropy is additive in nature. For example, if we will take two particles A and B which have entropy S_A and S_B. Then net entropy

$$S = S_A + S_B \tag{5.16}$$

Probability function is multiplicative in nature i.e.

$$f(w) = f(w_A.w_B) \tag{5.17}$$

Entropy can be represented as

$$S = f(w) = f(w_A.w_B) = f(w_A) + f(w_B) \tag{5.18}$$

Now taking the derivative of equation (5.18) w.r.t. w_B, we got

$$\frac{df(w)}{dw_B} = \frac{df(w_A)}{dw_B} + \frac{df(w_B)}{dw_B} \tag{5.19}$$

$$\Rightarrow \frac{df(w_A.w_B)}{d(w_A.w_B)} \times \frac{d(w_A.w_B)}{dw_B} = \frac{df(w_B)}{dw_B} \tag{5.20}$$

$$\Rightarrow w_A \frac{df(w_A.w_B)}{d(w_A.w_B)} = \frac{df(w_B)}{dw_B} \tag{5.21}$$

Now taking derivative of equation (5.21) w.r.t. w_A, we got

$$\left[w_A \frac{d\left(\frac{df(w_A.w_B)}{d(w_A.w_B)}\right)}{d(w_A.w_B)} \times \frac{d(w_A.w_B)}{dw_A}\right] + \left[\frac{df(w_A.w_B)}{d(w_A.w_B)} \times \frac{dw_A}{dw_A}\right] = \frac{d\left(\frac{df(w_B)}{dw_B}\right)}{dw_A} \tag{5.22}$$

$$\Rightarrow w_A.w_B \frac{d^2f(w_A.w_B)}{d(w_A.w_B)^2} + \frac{df(w_A.w_B)}{d(w_A.w_B)} = 0 \tag{5.23}$$

Putting $w_A.w_B = w$ in equation (5.23), we got

$$w\frac{d^2f(w)}{dw^2} + \frac{df(w)}{dw} = 0 \tag{5.24}$$

So, equation (5.24) became a 2nd order differential equation.

For 2nd order differential equation the solution is

$$f(w) = c_1 \ln w + c_2 \Rightarrow S = c_1 \ln w + c_2 \tag{5.25}$$

Now for no disorderness S=0, equation (5.25) became

$$c_1 \ln w + c_2 = 0 \tag{5.26}$$

Again as we have S=0 i.e. there is only one microstate is possible,$w \cong 1 \Rightarrow \ln w = 0$. Hence equation (5.26) will become

$$c_2 = 0 \tag{5.27}$$

Now taking

$$c_1 = \frac{R}{N_0} = k \tag{5.28}$$

[Where, R = Universal gas constant

N_0= Avogadro's number

K = Boltzmann's constant]

Now using the equation (5.27) and (5.28) in equation (5.25), we got

$$S = k \ln w \tag{5.29}$$

5.6 DEBYE AND EINSTEIN CONCEPT OF HEAT CAPACITY:

5.6.1 Heat Capacity of Ideal Gases:

From the Kinetic theory of gases, we have the following knowledge given below

Types of gases	Examples	c_v value	c_p value
Monatomic	He, Ne, Ar etc.	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	O_2,N_2,H_2 etc.	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic	O_3	$\frac{7}{2}R$	$\frac{9}{2}R$

5.6.2 Einstein's Theory of heat capacity of solids:

In early 20th century, Einstein represents the experimental datas of Cv of some solid elements using quantum theory.

Each atom in the crystal assumes to oscillate independently along three perpendicular directions under the harmonic motion i.e. to-fro motion. The energy of ith energy level of harmonic oscillation is given as

$$\varepsilon_i = \left(i + \frac{1}{2}\right) h\vartheta \tag{5.30}$$

Again, we know

$$U = 3 \sum n_i \varepsilon_i \tag{5.31}$$

Now combining equation (5.30) & (5.31), we have got

$$U = \frac{3}{2}N_o h\vartheta + \frac{3N_o h\vartheta}{\left(e^{h\vartheta/k_b T} - 1\right)} \tag{5.32}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3R\left(\frac{\theta_E}{T}\right)^2 \left(\frac{e^{\left(\theta_E/T\right)}}{\left(e^{\left(\theta_E/T\right)} - 1\right)^2}\right) \tag{5.33}$$

Where

$$\theta_E = \text{Einstain Temperature} = \frac{h\vartheta}{k_B} \tag{5.34}$$

5.6.3 Debye's Theory of Heat Capacity of Solids:

Einstein's deviation was to be later modified by Debye who assumed a spectrum of vibration frequency in contrast to a single frequency of oscillation of Einstein. Debye arrived at a different equation in terms of Debye temperature (θ_D). Where

$$\theta_D = \frac{h\vartheta_D}{k_B}\ ,\ \vartheta_D = \vartheta_{max} \tag{5.35}$$

At low temperature (near 0K), the Debye equation may be simplified as

$$C_V = 464.5 \times \left(T/\theta_D\right)^3 \tag{5.36}$$

Moreover it is concerned with elements only, that too in crystalline state. Hence, due to its limited applicability, it is a normal practice to determine heat capacity vs Temperature relationship for solids and liquids.

CHAPTER-6

FUGACITY

6.1 ESCAPING TENDENCY:

It is the tendency of dissolution of one phase to another phase on the measure of thermodynamic potential.

Let's consider a system consists of liquid phase and a gaseous phase of water. Then to express the escaping tendency or migration of molecules from one phase to another, thermodynamic parameter molar thermodynamic potential is used. In such cases, three cases arise

Case-1: When system is in equilibrium i. e. no migration of molecules from one phase to another, Hence

$$G_{\mathrm{vapour}} = G_{\mathrm{liquid}} \Rightarrow \overline{\Delta G} = 0 \tag{6.1}$$

Case-2: Temperature is slightly increased, as a result liquid molecules starts vaporizing then

$$G_{\mathrm{vapour}} < G_{\mathrm{liquid}} \Rightarrow \overline{\Delta G} = +\mathrm{ve} \tag{6.2}$$

Case-3: Suppose the temperature is lowered, n such case condensation of gas molecules starts. So in that case

$$G_{\mathrm{vapour}} > G_{\mathrm{liquid}} \Rightarrow \overline{\Delta G} = -\mathrm{ve} \tag{6.3}$$

6.2 FUGACITY:

At $P \to 0, \overline{G} = -\infty$ in this condition escaping tendency measure by a term known as fugacity.

Fugacity related with pressure under the mathematical expression mentioned below

$$f = Pe^{\left(-A/_{RT}\right)} \tag{6.4}$$

6.2.1 Graphical Representation of Fugacity:

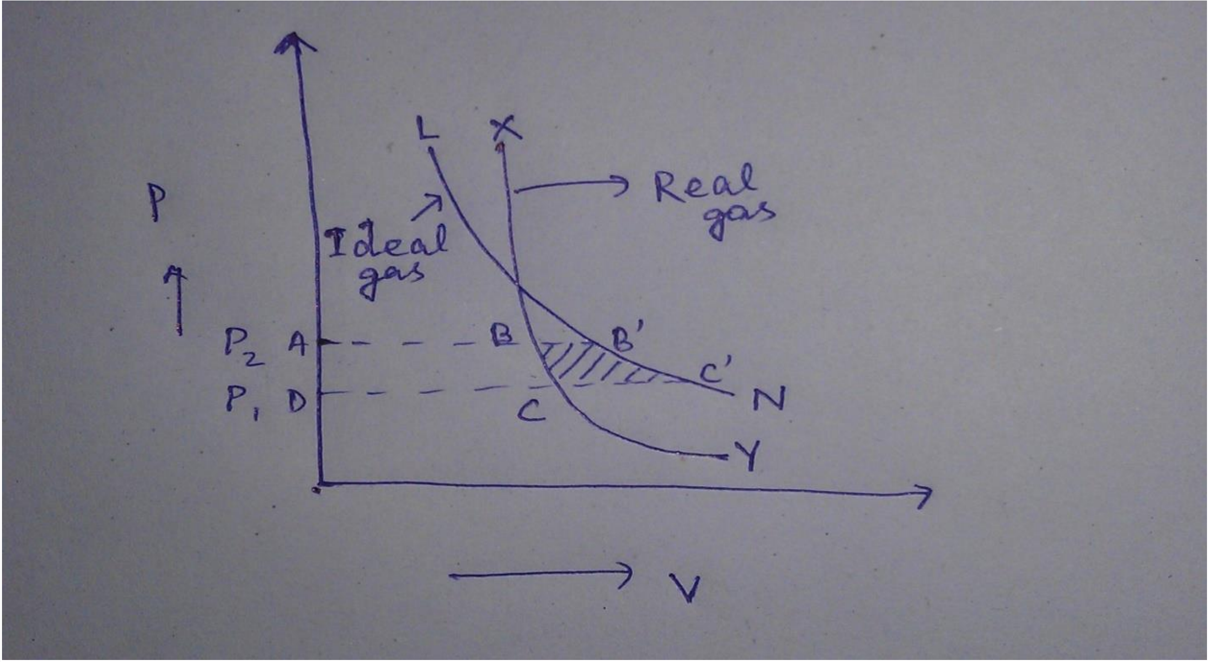

Fig 6.1 Combined Pressure vs. Volume graph for Ideal and Real gas

Since we know that

$$\mathrm{dG} = \mathrm{VdP} - \mathrm{SdP} \qquad (6.5)$$

At constant temperature

$$\mathrm{dG} = \mathrm{VdP} \qquad (6.6)$$

Now integrate from P_1 to P_2 pressure change

$$\int_{P_1}^{P_2} \mathrm{dG_{ideal}} = \mathrm{V}\int_{P_1}^{P_2} \mathrm{dP} = \text{Area A B}'\text{C}'\text{D} \qquad (6.7)$$

$$\int_{P_1}^{P_2} \mathrm{dG_{real}} = \mathrm{V}\int_{P_1}^{P_2} \mathrm{dP} = \text{Area A BCD} \qquad (6.8)$$

$$\int_{P_1}^{P_2} \mathrm{dG_{ideal}} = \int_{P_1}^{P_2} \mathrm{dG_{real}} - \mathrm{A}' \qquad (6.9)$$

For $P_1 \rightarrow 0, P_2 \rightarrow P$ then equation (5) becomes

$$\mathrm{G_{real}^{P}} = \mathrm{G_{ideal}^{P}} - \mathrm{A}' \qquad (6.10)$$

$$\Rightarrow \mathrm{RT\ln f} = \mathrm{RT\ln P} - \mathrm{A}' \qquad (6.11)$$

$$\Rightarrow f = Pe^{-A/RT} \qquad (6.12)$$

6.3 ARRHENIUS EQUATION:

The Arrhenius equation is a simple but remarkably accurate formula for the temperature dependence of reaction rates. The equation was proposed by Svante Arrhenius in 1889, based on the work of Dutch chemist Jacobus Henricus van 't Hoff who had noted in

1884 that Van 't Hoff's equation for the temperature dependence of equilibrium constants suggests such a formula for the rates of both forward and reverse reactions. Arrhenius provided a physical justification and interpretation for the formula.

Arrhenius' equation gives the dependence of the rate constant k of a chemical reaction on the absolute temperature T (in Kelvin), where A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant

$$\mathrm{K} = \mathrm{A}e^{-\left(\mathrm{E_a}/\mathrm{RT}\right)} \tag{6.13}$$

Arrhenius equation can also be represented as

$$\ln \mathrm{K} = \ln \mathrm{A} - \left(\mathrm{E_a}/\mathrm{RT}\right) \tag{6.14}$$

6.3.1 Activation Energy:

The existence of energy barrier between reactants and products is termed as activation energy.

From, Arrhenius equation if we will plot $\ln \mathrm{K}$ vs $\left(1/\mathrm{T}\right)$, then slope of the line will give $-\left(\mathrm{E_a}/\mathrm{RT}\right)$ from which activation energy can be calculated.

6.4 ACTIVITY:

The activity of a substance may be defined as the ratio of fugacity of the substance to the fugacity in its standard state.

Mathematically it can be represented as,'

$$a = \frac{f}{f^0} \tag{6.15}$$

At standard state, a=1, since $f = f^0$

Again for real gas,

$$\int_{G_i^0}^{G_i} dG_{real} = RT \int_{f_i^0}^{f_i} d\ln f \tag{6.16}$$

$$\Rightarrow G_i - G_i^0 = RT \ln\left(f_i/f_i^0\right) \tag{6.17}$$

Since $a_i = \frac{f_i}{f_i^0}$, so equation (6.17) becomes

$$\mathrm{G_i - G_i^0 = RT\ln a_i} \quad (6.18)$$

In an ideal gas mixture, $P_i = f_i$. Hence

$$G_i - G_i^0 = RT\ln(P_i - P_i^0) = RT\ln\left({}^{P_i}\!/_{P_i^0} \right) \quad (6.19)$$

Since $P_i^0 = 1\ atm$, So equation (6.19) becomes

$$G_i - G_i^0 = RT\ln P_i \text{ (Since } \ln P_i^0 = \ln 1 = 0) \quad (6.20)$$

From equation (6.18) and (6.20), we got

$$\mathrm{RT\ln a_i = RT\ln P_i \Rightarrow a_i = P_i} \quad (6.21)$$

N. B.:

- a_i is a dimensionless quantity.
- Value of a_i is numerically equal to the value of P_i (in atm).

6.5 EQUILIBRIUM CONSTANT:

Generally, Equilibrium constant for a chemical reaction given by 'K'.

6.5.1 Relationship of K with standard free energy of Reaction:

Consider the following reaction at constant temperature and pressure as

$$lL + mM + \cdots = qQ + rR + \cdots \quad (6.22)$$

[Where

l, m, q, r, …. represents number of moles

(L, M,…) and (Q, R,…) represents reactants and products respectively.]

Then

$$\Delta G = \left(qG_Q + rG_R + \cdots\right) - (lG_L + mG_M + \cdots) \quad (6.23)$$

$$\Delta G^0 = \left(qG_Q^0 + rG_R^0 + \cdots\right) - (lG_L^0 + mG_M^0 + \cdots) \quad (6.24)$$

$$\Delta G - \Delta G^0 = \left[q\left(G_Q - G_Q^0\right) + r(G_R - G_R^0) + \cdots\right] - [l(G_L - G_L^0) + m(G_M - G_M^0) + \cdots] \quad (6.25)$$

Since we know,

$$G_i - G_i^0 = RT\ln a_i \tag{6.26}$$

So equation (6.26) becomes

$$\Delta G - \Delta G^0 = RT\big[\big(q\ln a_Q + r\ln a_R + \cdots\big) - \left(l\ln a_L + m\ln a_M + \cdots\right)\big] \tag{6.27}$$

$$\Rightarrow \Delta G - \Delta G^0 = RT\ln\left[\frac{a_Q^q . a_R^r \ldots\ldots}{a_L^l . a_M^m \ldots\ldots}\right] = RT\ln J \tag{6.28}$$

Where

$$J = Activity\ questient\ = \left[\frac{a_Q^q . a_R^r \ldots\ldots}{a_L^l . a_M^m \ldots\ldots}\right] \tag{6.29}$$

At equilibrium,

$$(\Delta G)_{P,T} = 0 \tag{6.30}$$

So equation (6.28) becomes

$$-G^0 = RT\ln[J]_{At\ equilibrium} = RT\ln K$$

$$\Rightarrow \Delta G^0 = RT\ln K \tag{6.31}$$

Replacing equation (6.31) in equation (6.28) we have

$$\Delta G - (-RT\ln K) = RT\ln J$$

$$\Rightarrow \Delta G = RT\ln J - RT\ln K = RT\ln\left(\frac{J}{K}\right) \tag{6.32}$$

N. B.:

For Isothermal process,

$$\Delta G = \Delta H - T\Delta S \tag{6.33}$$

Therefore

$$\Delta \mathrm{G}_\mathrm{f}^0(\mathrm{T}) = \Delta \mathrm{H}_\mathrm{f}^0(\mathrm{T}) - \mathrm{T}\Delta \mathrm{S}_\mathrm{f}^0(\mathrm{T}) \tag{6.34}$$

Now from Kirchhoff's law

$$\mathrm{H}_\mathrm{T}^0 = \mathrm{H}_{298}^0 + \int_{298}^{\mathrm{T}} \Delta \mathrm{C}_\mathrm{P}^0 \mathrm{dT}$$

$$\Rightarrow \Delta \mathrm{H}_\mathrm{f}^0(\mathrm{T}) = \Delta \mathrm{H}_\mathrm{f}^0(298) + \int_{298}^{\mathrm{T}} \Delta \mathrm{C}_\mathrm{P}^0\, \mathrm{dT} \tag{6.35}$$

Again

$$\Delta \mathrm{S}_\mathrm{f}^0(\mathrm{T}) = \Delta \mathrm{S}_\mathrm{f}^0(298) + \int_{298}^{\mathrm{T}} \frac{\mathrm{C}_\mathrm{P}^0}{\mathrm{T}}\, \mathrm{dT} \tag{6.36}$$

Using equation (6.35) and (6.36) in equation (6.34), we have

$$\Delta G_f^0(T) = \left[\Delta H_f^0(298) + \int_{298}^{T} \Delta C_P^0 dT\right] - T\left[\Delta S_f^0(298) + \int_{298}^{T} \frac{\Delta C_P^0}{T} dT\right] \qquad (6.37)$$

For pure elements, $H_{298}^0 = 0$, but $S_{298}^0 \neq 0$.

6.6 USE OF S FUNCTION:

In the following area S – function is used

1. In Nozzle and Diffuser.
2. In Throttling device.
3. In Turbine and Compressors.
4. In heat exchangers.
5. In Carnot Engine.
6. In Refrigerator.

6.7 ELLINGHAM – RICHARDSON DIAGRAM:

- R-E diagram is the simplest method of representing free energy vs Temperature for compounds such as oxides and sulphides.

- Temperature change in ΔH^0 and ΔS^0 tends to counterbalance each other. Therefore it is possible to express ΔG^0 in the form of a simple equation

$$\Delta G^0 = a - bT \qquad (6.38)$$

[Where a and b are mean values of ΔH^0 and ΔS^0 for temperature range under consideration]

- In this diagram, highly stable oxides are found at the bottom and less stable oxides occupy higher positions. Therefore, an element present at the lower position will always reduce the oxides of another metal lying above it, when all the reactants and products are in their standard states.
- In the regions, since no phase transformation occur. So plots are almost straight lines.
- Since ${d\Delta G^0}/{dT} = -\Delta S^0$, slope of the line gives $-\Delta S^0$ and extrapolated the plot to absolute zero gives intercept of line ΔH^0 on free energy axis.
- Since free energy is an extensive property. Hence the value of ΔG of a reaction would depend on number of moles involved.

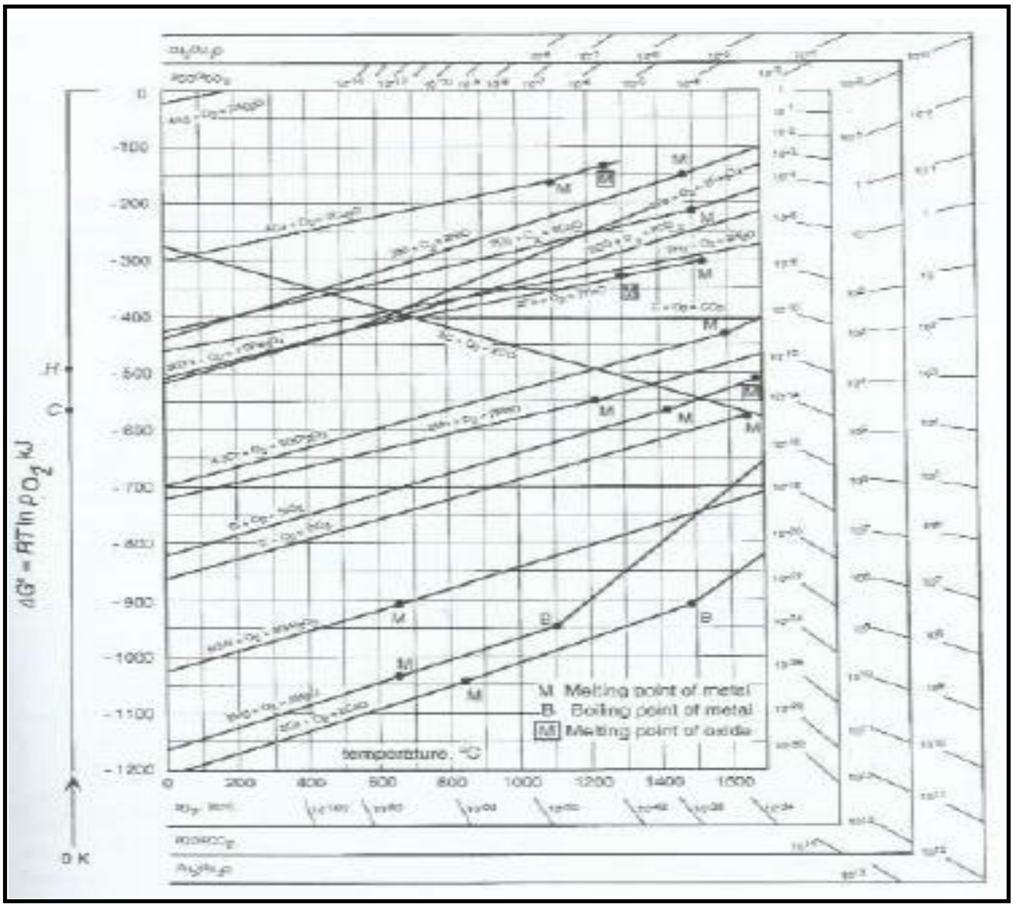

Fig-6.2 Ellingham Diagram of Selected Oxides

6.7.1 Characteristics of R-E Diagram:

i. Different metals & its oxides of metallurgical processes are available in R-E diagram.

ii. The zero free energy is at the top of the diagram & towards down in the Y-axis is negative value is represented.

iii. This is a standard diagram because the reactant which are metal and products which are oxides in general are in their standard state i.e. unity activity.

iv. Oxides or compounds which are placed at bottom of the graph indicate more negative free energy i.e. is more stable & they reduce the less stable oxides that placed above it.

v. Change in slope indicates phase transformation from one phase to another phase.
   a. Increase in slope indicates reactant undergoing phase transformation.
   b. Decrease in slope indicates product undergoing phase transformation.
   c. Large slope change indicates transformation from condensed phase to gaseous phase.

   d. Small slope phase change indicates melting or change of solid to other phase.
   e. No change in slope indicates no phase transformation.

vi. Almost all oxides have negative free energy. However, for noble metal case there is some exception.

vii. The line for CO_2 would almost parallel to the temperature axis indicates the value ΔS^0 almost zero.

viii. Upward slope of most of lines indicates that the oxides become less stable as the temperature increases.

ix. The reaction $2C_{(S)} + O_{2(g)} = 2CO_{(g)}$ extremely important since in this case it has downward slope cutting across the free energy diagram. This indicates, why that all metal oxides can be reduced by CO above 1000^0 C.

x. Below 1000^0 C, $2CO_{(g)} = 2CO_{2(g)} + C_{(s)}$ occur. So below 1000^0 C carbon monoxide is unstable.

Limitations:

a. Both products and reactants are in the standard state (i. e. pure substance at 1 atm).
b. No Ellingham diagram for solution because thermodynamic activity data are required.
c. No reaction then difficult to predict the rate of reaction.

CHAPTER-7

THERMODYNAMICS OF SOLUTIONS

7.1 IDEAL & NON-IDEAL SOLUTIONS:

Consider the vaporization of a component ‘A’ from a liquid solution at temp. T. if the vapor behaves as ideal gas, then the equilibrium constant is given as

$$\mathrm{K} = {}^{\mathrm{P_A}}\!/\!{}_{\mathrm{a_A}} = \mathrm{P_A^0} \tag{7.1}$$

The above process can be expressed as

Reaction 7.1: $A(liquid) \rightarrow A(solid)$

Equilibrium constant can be calculated for above reaction as

$$\mathrm{K} = \left[\frac{\text{Activity of product (vapour)}}{\text{Activity of reactant(Liquid)}}\right]_{\text{at eqlbm}} = \frac{\mathrm{P_A}}{\mathrm{a_A}} \tag{7.2}$$

(Since ideal gas mixture case a=P)

Again we have, P_a = Vapour pressure of A in the solution i.e. A+B (A <100%)

P_A^0 = vapour pressure of pure A i.e. only A i.e. 100%A

For pure A case i.e. only A is there then

$$a_A = 1 \qquad \& \qquad P_A = P_A^0 \tag{7.3}$$

From above equation (7.1), we have

$$a_A = \frac{P_A}{P_A^0} \tag{7.4}$$

Now taking the temperature as T, Let us consider there are two closed containers out of which one contains a liquid solution, where A is the component & another contains pure A. So if in case of solution the vapour pressure is P_A & in case of pure A the vapour pressure is P_A^0. Then for solution case, we can have expressed the mole fraction of component ‘A’ as

$$X_A = \text{mole fraction of A in the solution} = {}^{P_A}\!/\!{}_{P_A^0} \tag{7.5}$$

Now, from equation (7.4) & (7.5), we have

$$a_A = x_A \tag{7.6}$$

If the solution obeys Raoult's law then it is called an ideal solution & if the solution does not obey Raoult's law then it is called non-ideal solution.

There is a term known as activity co-efficient (γ) & mathematically it represented as

$$\gamma_\mathrm{i} = \frac{\text{activity of the component}}{\text{Mole fraction of the component}} = \frac{\mathrm{a_i}}{\mathrm{x_i}} \qquad (7.7)$$

$$\Rightarrow a_i = \gamma_{i.}x_i \qquad (7.8)$$

[Where γ^i - Activity co-efficient of component in a solution]

Now, if in a solution,

a. $\gamma^i = 1$, solution is ideal.
b. $\gamma^i > 1$, solution exhibits positive departure from Raoult's law.
c. $\gamma^i < 1$, solution exhibits negative departure from Raoult's law.

In a solution, $a_i < 1$, in contrast to pure i where $a_i = 1$. This difference is due to the following two effects

i. Dilution of component i in a solution due to the presence of other component (dilution effect).
ii. Interaction of component i with other components in a solution (interaction effect).

7.1.1 Activity:

It is measure of free concentration i.e. concentration available for reaction.

In an ideal solution, the entire concentration is available i.e. there is only dilution effect.

In case of binary solution like A-B, interaction effect more easily followed. There is mainly three types of bonds between atoms (or molecules) of A & B such as A – A and B – B are like bonds & A –B is unlike bond.

i. If A – B bond stronger than the average of A – A & B – B bonds i.e. A & B have the tendency to form a compound, then less numbers of A & B atoms remains free. In this case the solution exhibit negative departure from the Raoult's law i.e. $\gamma_A < 1$, $\gamma_B < 1$.
ii. If A –A & B – B bonds average is greater than A – B bonds then atoms (or molecules) have the tendency more to form clusters. In this case the solution would exhibit's positive departure from Raoult's law.

Examples:

- Ideal solution: Cu – Ag, Fe – Ni, Fe – Mn, FeO – MnO.
- Negative Departure from Raoult's Law: Silicates such as CaO – SiO_2 & MnO – SiO_2.
- Positive Departure from Raoult's Law: Cu – Fe.

7.2 PARTIAL AND INTEGRAL MOLAR QUANTITIES:

For a closed system, where there is no possibility of mass and concentration change, change of the components present in the system and the Thermodynamic properties mainly depends on P, V and T, where as in case of open system Thermodynamic properties essentially depends on P, V, T and mass of the system.

Let X be the Thermodynamic property

Case-1 (In case of closed system):

$$X_1^{'} = f(P,V) \tag{7.9}$$

$$X_2^{'} = f(T,V) \tag{7.10}$$

$$X_3^{'} = f(P,T) \tag{7.11}$$

Case-II (In case of Open system):

Open system in which and chemical composition may change, the extensive properties i. e. U, G, S, V, H etc must depends on the amount of composition present in the system.

So any extensive properties

$$X^{'} = f(P,T,n_1,n_2,\dots,n_i) \tag{7.12}$$

Where $n_1, n_2, \dots, n_i$ are number of moles of the 1^{st}, 2^{nd}, … , ith component in the system present as gm/mol.

Let us consider, there is a very small change in all the variables in all the systems.

$$\mathrm{dX}' = \left(\frac{\partial \mathrm{X}}{\partial \mathrm{P}}\right)_{\mathrm{T},\mathrm{n}_1,\mathrm{n}_2,\dots,\mathrm{n}_\mathrm{i}} \partial\mathrm{P} + \left(\frac{\partial \mathrm{X}}{\partial \mathrm{T}}\right)_{\mathrm{P},\mathrm{n}_1,\mathrm{n}_2,\dots,\mathrm{n}_\mathrm{i}} \partial\mathrm{T} + \left(\frac{\partial \mathrm{X}}{\partial \mathrm{n}_1}\right)_{\mathrm{P},\mathrm{T},\mathrm{n}_2,\dots,\mathrm{n}_\mathrm{i}} \partial\mathrm{n}_1 + \left(\frac{\partial \mathrm{X}}{\partial \mathrm{n}_2}\right)_{\mathrm{P},\mathrm{T},\mathrm{n}_1,\dots,\mathrm{n}_\mathrm{i}} \partial\mathrm{n}_2 + \cdots + \left(\frac{\partial \mathrm{X}}{\partial \mathrm{n}_\mathrm{i}}\right)_{\mathrm{P},\mathrm{T},\mathrm{n}_1,\dots,\mathrm{n}_{\mathrm{i}-1}} \partial\mathrm{n}_\mathrm{i} \tag{7.13}$$

From the above relation, we have

$$\boxed{\begin{array}{c} \overline{X_1} = \left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,\dots,n_i} \\ \overline{X_2} = \left(\frac{\partial X}{\partial n_2}\right)_{P,T,n_1,\dots,n_i} \\ \cdot \\ \cdot \\ \cdot \\ \overline{X_i} = \left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_1,\dots,n_{i-1}} \end{array}} \qquad (7.14)$$

Rate of change of Thermodynamic properties on addition of 1 mole of the component when all other variables are unchanged. So we have at constant P, T equation (7.14) becomes

$$dX' = \overline{X_1}dn_1 + \overline{X_2}dn_2 + \cdots + \overline{X_i}dn_i = \sum_i \overline{X_i}dn_i \qquad (7.15)$$

Now if X mean to molar properties of a solution. Then X' i. e. the value of quantity X for the entire solution given by

$$X' = n_T X \Rightarrow dX' = n_T dX \qquad (7.16)$$

[Where

$n_T = \sum_i n_i = n_1 + n_2 + \cdots + n_i$

X – Integral molar value of X in the solution]

Now from equation (7.15) and (7.16), we will have

$$\sum_i \overline{X_i}\, dn_i = n_T dX \qquad (7.17)$$

$$\Rightarrow dX = \sum_i \overline{X_i}\frac{dn_i}{n_T} = \sum_i \overline{X_i}\, dX_i \qquad (7.18)$$

[Where

$dX_i = \frac{dn_i}{n_T} =$ Mole fraction of component i in the solution

dX – Integral molar value of the solution

$\overline{X_i}$ – Partial molar value of X' of component i in the solution]

7.3 GIBBS – DUHEM EQUATION [PARTIAL & INTEGRAL MOLAR PROPERTIES]:

7.3.1 Relations amongst partial molar properties:

Imagine a very large quantity of solution, add 1 gm-mole of pure i into it. Upon dissolution, the total quantity of solution increase by 1 gm – mole. As a result without effective the composition so much the Q get increases. For constant pressure & temperature the increase in Q' is equal to $\bar{Q}_i$. Therefore, $\bar{Q}_i$ .is the value of Q per mole of i in the solution

Again, we know

$$\overline{Q_i}^m = \bar{Q}_i - Q_i^0 \tag{7.19}$$

[Where

$Q_i^0 = Q$ per mole for pure i

$\overline{Q_i^m}$ = Partial molar value of Q of mixture of i in the solution

$\bar{Q}_i$ = Partial molar value of Q of component in the solution]

So for Gibbs free energy per gm. mole of component i, we have

$$\overline{G_i}^m = \bar{G}_i - G_i^0 \tag{7.20}$$

Again in general,

$$\overline{dH_i} = T\,\overline{ds_i} + \bar{V}_i dP \tag{7.21}$$

$$\overline{dG_i} = -\bar{S}_i\,dT + \bar{V}_i\,dP \tag{7.22}$$

$$\overline{dH_m} = T\,\overline{dS_i^m} + \overline{V_i^m}\,dP \tag{7.23}$$

$$\overline{dG_i^m} = -\overline{S_i^m}dT + \overline{V_i^m}\,dP \tag{7.24}$$

So, we have

$$\bar{G}_i = \overline{H_i} - T\bar{S}_i \tag{7.25}$$

$$G_i^0 = H_i^0 - TS_i^0 \tag{7.26}$$

$$\overline{G_i^m} = \overline{H_i^m} - T\overline{S_m} \tag{7.27}$$

Using equation (7.25) and (7.26) in equation (7.20), we will get equation (7.27) as follows

$$\overline{G_i^m} = \overline{G_i} - G_i^0 = (\overline{H_i} - T\,\bar{S}_i) - (H_i^0 - TS_i^0) \tag{7.28}$$

$$\Rightarrow \overline{G_i^m} = (\overline{H_i} - H_i^0) - (T\bar{S}_i - TS_i^0) = \overline{H_i^0} - T\overline{S_i^0} \tag{7.29}$$

So considering some common extensive properties, we can write

$$\overline{G_i'} = \left(\frac{\partial G'}{\partial \eta_i}\right) \text{T, P, } n_1, n_2 \ldots \text{ except } n_i \tag{7.30}$$

$$\overline{S_i} = \left(\frac{\partial S'}{\partial \eta_i}\right) \text{T, P, } n_1, n_2 \ldots \text{ except } n_i \tag{7.31}$$

$$\overline{H_i} = \left(\frac{\partial H'}{\partial \eta_i}\right) \text{T, P, } n_1, n_2 \ldots \text{ except } n_i \tag{7.32}$$

$$\overline{V_i} = \left(\frac{\partial V'}{\partial \eta_i}\right) \text{T, P, } n_1, n_2 \ldots \text{ except } n_i \tag{7.33}$$

Again, using equation (7.19), we can get the following equations

$$\overline{G_i^m} = \overline{G_i} - G_i^0 \tag{7.34}$$

$$\overline{S_i^m} = \overline{S_i} - S_i^0 \tag{7.35}$$

$$\overline{H_i^m} = \overline{H_i} - H_i^0 \tag{7.36}$$

$$\overline{V_i^m} = \overline{V_i} - V_i^0 \tag{7.37}$$

Common symbols that are used

Q – Extensive property of solution, it can refer as U, H, V, S, G etc.

$\overline{Q_i}$ - Partial molar value of Q of component i in the solution.

Q_i^0 - Q per mole for pure i.

$\overline{Q_i^m}$ - Partial molar value of mixing of component i in the solution.

Q' - Value of quantity in the entire solution

7.3.2 **Gibb's – Duhem Equation:**

Since we know, at constant T, P we have got

$$\partial Q' = \overline{Q_1}\,\partial n_1 + \overline{Q_2}\,\partial n_2 + ----+ \overline{Q_n}\,\partial n_n \tag{7.38}$$

$$\Rightarrow \partial Q' = \textstyle\sum_i \overline{Q_i}\,\partial n_i \tag{7.39}$$

By adding small quantities of component $(\partial n_1, \partial n_2, \ldots, \partial n_i)$ at constant T, P such that overall composition of the solution remains same in all stages. Since $\overline{Q_1}$, $\overline{Q_2}$, ………., $\overline{Q_i}$ are functions of T, P & compositions. So these are remained constant. Therefore after the additions are complete, we get

$$Q' = \overline{Q_1}n_1 + \overline{Q_2}n_2 + \ldots\ldots\ldots\ldots + \overline{Q_n}n_n \tag{7.40}$$

Differentiating equation (7.40), we will get

$$dQ' = (\overline{Q_1}dn_1 + n_1\overline{dQ_1}) + (\overline{Q_2}dn_2 + n_2\overline{dQ_2}) + \ldots\ldots\ldots\ldots\ldots + \overline{(Q_n dn_n + n_n dQ_n)} \tag{7.41}$$

$$\Rightarrow dQ' = \textstyle\sum_i \overline{Q_i}dn_i + \sum_i n_i\overline{dQ_i} \tag{7.42}$$

Equating equation (7.39) and (7.42), we will get

$$\sum_i n_i \overline{dQ_\iota} = 0 \tag{7.43}$$

Dividing the equation (7.43) by the total no. of moles(n_T), we will get

$$\sum_i X_i \overline{dQ_\iota} = 0 \qquad \text{(Since, } \frac{n_i}{n_T} = X_i\text{)} \tag{7.44}$$

[Where, Total no of moles $(n_T) = n_1 + n_2 + \dots\dots\dots. + n_i$]

In the above, equation (7.43) and (7.44) are the alternative forms of **Gibb's-Duhem equation (G-H equation)**, which provide the principal foundation to thermodynamic solutions.

For Gibb's free energy, the G-H equation can be written as

$$\sum_i n_i \overline{dG_\iota} = 0 \qquad \text{Or} \qquad \sum_i X_i \overline{dG_\iota} = 0 \tag{7.45}$$

For pure component the values of Q such as $Q_1^0, Q_2^0, \dots\dots\dots, Q_i^0$ are constants at constant T & P. So $dQ_1^0, dQ_2^0, \dots\dots\dots\dots., dQ_i^0$ are zero. Hence we have

$$\sum_i n_i\, dQ_i{=}0 \qquad \text{or} \qquad \sum_i X_i\, dQ_i{=}0 \tag{7.46}$$

Since we know that

$$\sum_i n_i \overline{dQ_\iota^m} = \sum_i n_i d(\overline{Q_\iota^m} - Q^0) = 0$$

Or

$$\sum_i X_i \overline{dQ_\iota^m} = \sum_i X_i d(\overline{Q_\iota^m} - Q^0) = 0 \tag{7.47}$$

7.4 ACTIVITY VS MOLE FRACTION (HENRY'S LAW):

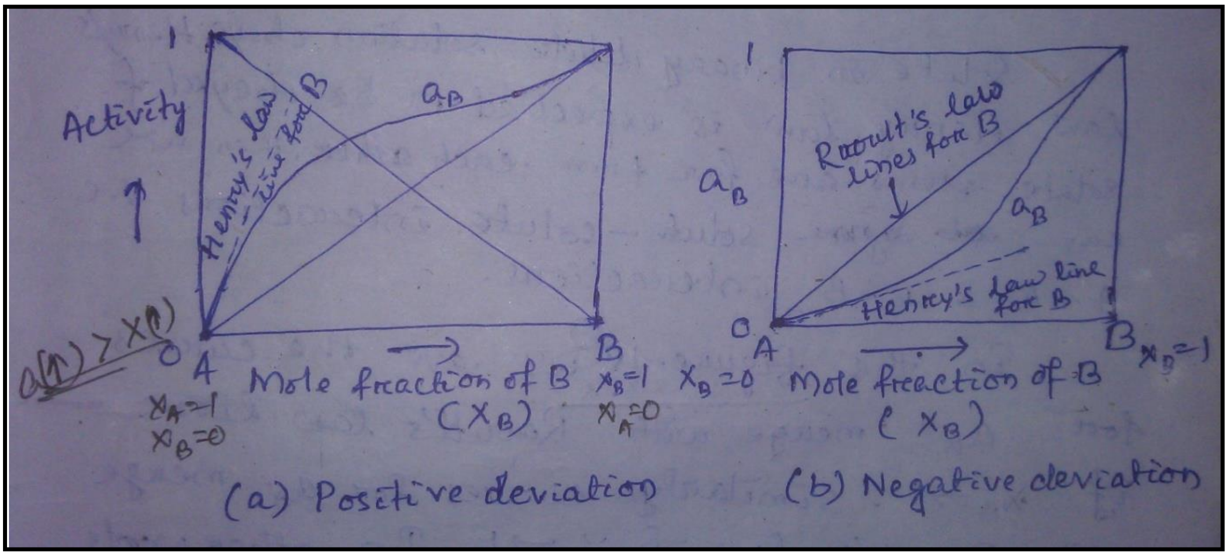

Fig 7.1: (a) Positive & (b) Negative deviations from the Raoult's law for component B in the binary A-B solution; Henry's law lines for B are also shown.

The above Fig 7.1 represents activity Vs mole fraction curves for binary A-B solutions at constant temperature. It shows Raoult's law line component A & B. Positive & negative departures from Raoult's law are illustrated for a_B with X_B is leaner. This is basis for Henry's law for binary solution.

Henry's law stated as, if $x_B \rightarrow 0$, then $\gamma_B \rightarrow a$ constant γ_B^0. In other words, in Henry's law region for B.

$$a_B = \gamma_B^0 x_B \tag{7.48}$$

[Where B is solute & A is solvent]

Similarly to equation (7.48), we will also have

$$a_A = \gamma_A^0 x_A \tag{7.49}$$

Solute in binary dilute solution obeys Henry's Law. Henry's law is expected to be obeyed if solute atoms are far from each other then we can ignore solute-solute interaction i.e. A-A & B-B interactions.

In the Fig. 1 & 2, we have the curves for a_B merge with Raoult's law line if $x_B \rightarrow 1$. In other words, in the region where B obeys Henry's law, A tends to obey Raoult's law & Vice versa.

7.4.1 Proof of the Above Statement:

From the Gibb's-Duhem equation, we have

$$x_A \overline{dG_A^m} + x_B dG_B^m = 0 \tag{7.50}$$

$$\Rightarrow RT[x_A d(lna_A) + x_B d(lna_B)] = 0 \tag{7.51}$$

$$\Rightarrow RT\, x_A\, d\, lna_A + RT\, x_B\, d\, lna_B = 0 \tag{7.52}$$

$$\Rightarrow x_A\, d\, lna_A = -\, x_B\, d\, lna_B \tag{7.53}$$

$$\Rightarrow d\, lna_A = -\, \frac{x_B}{x_A} d\, lna_B \tag{7.54}$$

If B obeys Henry's law, then

$$d\,(lna_B) = d[\ln(\gamma_B^0 x_B) = d\,[\ln \gamma_B^0 + lnx_B] \tag{7.55}$$

$[a_B = \gamma_B^0 x_B$ From equation (7.48)]

$$\Rightarrow d(\ln a_B) = d\ln\gamma_B^0 + d\ln x_B \quad (7.56)$$

$$\Rightarrow d\ln a_B = d\ln x_B \quad (7.57)$$

[Since $d\ln\gamma_B^0 = 0$ as γ_B^0 is constant]

Now from equation (7.54), we have

$$d\,lna_A = -\frac{x_B}{x_A} d\,lnx_B \quad (7.58)$$

$$\Rightarrow d(\ln a_A) = -\frac{x_B}{x_A}\frac{dx_B}{x_B} \quad (7.59)$$

$$\Rightarrow \mathrm{d}(\ln \mathrm{a_A}) = -\frac{dx_B}{x_A} \quad (7.60)$$

[Since $\frac{d\ln x}{dx} = \frac{1}{x} \Rightarrow dlnx = \frac{dx}{x}$]

Again we know,

$$dx_A + dx_B = 0 \;\; (Since\; x_A + x_B = 1) \quad (7.61)$$

$$\Rightarrow dx_B = -dx_A \quad (7.62)$$

So, using equation (7.62) in equation (7.60), we will get

$$d(lna_A) = \frac{dx_A}{x_A} = d\ln x_A \quad (7.63)$$

Taking integration of equation (7.63), we have

$$\ln a_A = \ln x_A + Constant \quad (7.64)$$

Let's consider I as a constant, then $\ln I$ will also a constant. Therefore, we can write equation (7.64) as

$$\Rightarrow \ln a_A = \ln X_A + \ln I \quad (7.65)$$

$$\Rightarrow \ln a_A = \ln(Ix_A) \quad (7.66)$$

$$\Rightarrow a_A = Ix_A \quad (7.67)$$

At $x_A \to 1, a_A \to 1$. Hence $I = 1$

Hence, equation (7.67) will become

$$a_A = x_A \quad (7.68)$$

i.e. A obeys Raoult's law when B obeys Henry's law.

7.5 REGULAR SOLUTIONS:

Since most of the solutions are non-ideal so there is a great need to express the thermodynamic quantity in these solutions in the form of analytical equations i.e. function of temperature & composition.

Regular solution model first proposed by Hildebrand, on approximation the model is not much more consistent. Hildebrand defined a regular solution as one in which

$$\overline{S_i}^{m} = \overline{S_i}^{m,id} \text{ But } \overline{H_i^m} \neq 0 \tag{7.69}$$

$$\text{i.e. } \Delta s^m = \Delta s^{m,id} \text{ But } \Delta H^m \neq 0 \tag{7.70}$$

[Where “id” subscript refers to ideal solution]

In other words, a regular solution has the same entropy as an ideal solution of same composition, but entropy is different from ideal solution.

7.5.1 Excess Function:

For dealing with non-ideal solutions, a function known as excess function (or molar excess property) used. It is only for extensive properties & defined as

$$Q^{xs} = Q - Q^{id} \tag{7.71}$$

Similarly, for partial molar excess properties the equation (7.71) will become

$$\overline{Q_i^{xs}} = \overline{Q_i} - \overline{Q_i^{id}} \tag{7.72}$$

[Here,

Q – Some extensive property (G, H, S……..) of the actual solution.

Q^{id} - Value of Q for ideal solution at same composition & temperature.

Q^{xs} - Value of Q in excess of that of ideal solution.]

For standard state, we can write equation (7.71) and (7.72) as

$$Q^{xs} = (Q - Q^0) \tag{7.73}$$

$$\Rightarrow Q^{XS} = \Delta Q^m - \Delta Q^{m,id} \tag{7.74}$$

$$\overline{Q^{xs}} = (\overline{Q_i} - Q_i^0) - (\overline{Q_i^{id}} - Q_i^0) \tag{7.75}$$

$$\Rightarrow \overline{Q_i^{XS}} = \overline{Q_i^m} - \overline{Q_i^{m,id}} \tag{7.76}$$

[Since, Q^0 is added & Q^0 subtracted. So, equation (7.74) & (7.76) are same as equation (7.71) & (7.72) respectively.

Hence, for a regular solution

$$\overline{G_i^{xs}} = \overline{H_i^{xs}} - T\overline{S_i^{xs}} = \overline{H_i^{xs}} = \overline{H_i^m} \tag{7.77}$$

$$G^{xs} = \Delta H^m \tag{7.78}$$

[Since for a regular solution no excess entropy i.e.$\overline{S_i^{xs}} = 0$, $S^{xs} = 0$.

Also $\overline{H_i^{xs}} = \overline{H_i^{m}}$, $H^{xs} = \Delta H^{m}$]

Again,

$$G^{xs} = \Delta G^{m} - \Delta G^{m,id} = RT\ \sum_i x_i\, ln a_i - RT\ \sum_i x_i \ln x_i = RT\ \sum_i x_i\, ln\gamma_i \qquad (7.79)$$

[Since, for ideal solution ($a_i = x_i$)]

7.5.2 Regular Binary Solutions:

For binary solution case, we have defined a function α that is given by

$$\alpha_i = \frac{\ln\gamma_i}{(1-x_{i)})^2} \qquad (7.80)$$

So, for A-B solution

$$\alpha_B = \frac{\ln\gamma_B}{(1-x_{B)})^2} = \frac{\ln\gamma_B}{x_A^2} \qquad (7.81)$$

$$\Rightarrow \ln\gamma_B = \alpha_B x_A^2 \qquad (7.82)$$

Similarly,

$$ln x_A = \alpha_A x_B^2 \qquad (7.83)$$

For binary regular solution

$$\alpha_A = \alpha_B = \alpha = \text{Constant} \qquad (7.84)$$

Since we know

$$\Delta H^{m} = G^{xs} = RT\ (x_A \ln\gamma_A + x_B \ln\gamma_B) \qquad (7.85)$$

$$\Rightarrow \Delta H^{m} = RT(\ x_A\alpha_A x_B^2 +\ x_B\alpha_B\ x_A^2) \qquad (7.86)$$

$$\Rightarrow \Delta H^{m} = RT\alpha\ (x_A x_B^2 +\ x_B\ x_A^2) \quad \text{(Using equation (7.84))} \qquad (7.87)$$

$$\Rightarrow \Delta H^{m} = RT\alpha x_A x_B(x_A +\ x_B) \qquad (7.88)$$

$$\Rightarrow \Delta H^{m} = RT\alpha X_A X_B \qquad (Since\ x_A +\ x_B = 1) \qquad (7.89)$$

$$\Rightarrow \Delta H^{m} = \Omega\, x_A x_B \qquad \text{(Since } \Omega = RT\alpha\text{)} \qquad (7.90)$$

[Where Ω is a parameter related to interaction energies in the solution]

Again, we have

$$\overline{H_A^{m}} = \overline{G_A^{xs}} = RT \ln\gamma_A = RT\alpha x_B^2 = \Omega x_B^2 \qquad (7.91)$$

$$\overline{H_B^{m}} = \overline{G_B^{xs}} = RT \ln\gamma_B = RT\alpha x_A^2 = \Omega x_A^2 \qquad (7.92)$$

ΔH^{m}, $\overline{H_i^{m}}$ of solutions mainly constant over a limited range approximately. So Ω assumed to be independent of temperature.

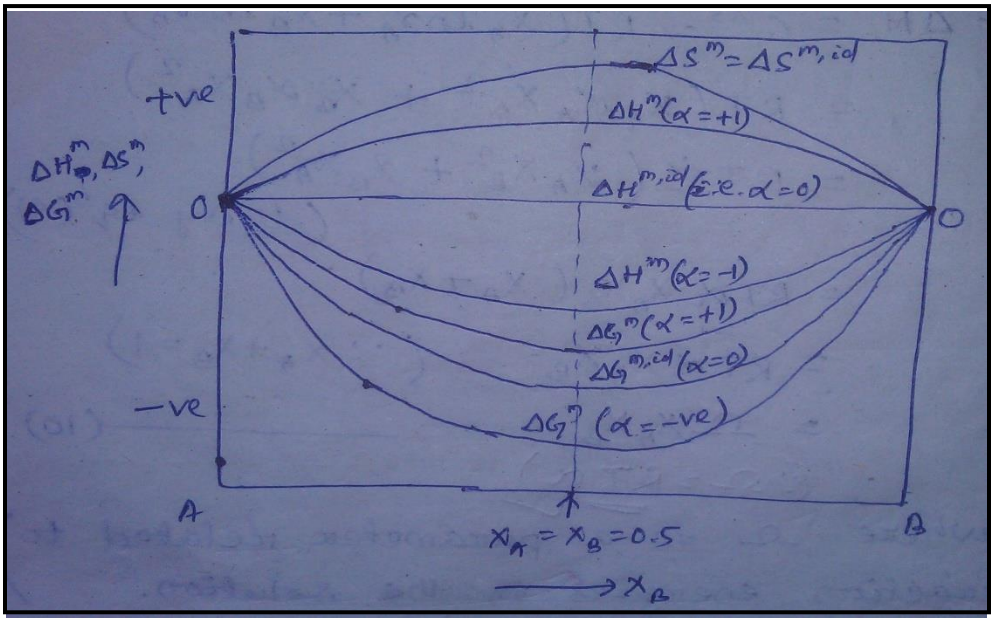

Fig 7.2: Graph shows changes of Enthalpy, Entropy & Free energy with mole fraction.

Therefore

$$\alpha = \frac{\Omega}{RT} \Rightarrow \alpha \propto \frac{1}{T} \tag{7.93}$$

i.e. α is inversely proportional to the temperature

- If $\Delta H^m = +ve, \alpha = +ve, \gamma_A > 1, \quad \gamma_B > 1$ ⇒+ve departure from Raoult's law.
- If $\Delta H^m = -ve, \alpha = -ve, \gamma_A < 1, \quad \gamma_B < 1$ ⇒-ve departure from Raoult's law.

7.6 QUASI-CHEMICAL APPROACH TO SOLUTIONS:

Thermodynamics properties of solutions are consequence of interaction amongst atoms molecules. Quasi-chemical theory is the simplest & able to explain the properties approximately from atomistic point of view.

In a metallic solution, the components are assumed to be present as atoms & not molecules due to nature of metallic bonds. So there exit interaction energy between them. The quasi-chemical theory explained by considering some important assumptions.

i. Atoms have chemical bonds amongst them.
ii. Bonds get associated with some enthalpy which alone contributes to enthalpy of solution.
iii. Only bonds amongst nearest neighboring atoms are energetically significant.

In, a binary A-B system, the bonds are A-A, B-B & A-B type. Assume that enthalpies associated with these bonds are H_{AA}, H_{BB} & H_{AB} respectively.

Let us consider one gm-atom of the solution. Let it have P_{AA}, P_{BB} & P_{AB} numbers of A-A, B-B and A-B bonds respectively. Then enthalpy of formation of the solution for one gm-atom from gasesous state at temperature T is

$$H = P_{AA}H_{AA} + P_{BB}H_{BB} + P_{AB}H_{AB} \tag{7.94}$$

If number of A atoms is N_A & B atomsN_B, Then

$$N_A = \frac{P_{AB}}{Z} + \frac{2P_{AA}}{Z} \tag{7.95}$$

$$N_B = \frac{P_{AB}}{Z} + \frac{2P_{BB}}{Z} \tag{7.96}$$

[Where Z – Coordination number]

Thus P_{AA} & P_{BB} can be expressed in terms of P_{AB},N_A, N_B and Z. Substituting these terms in the equation (7.94), we will get

$$H = \frac{1}{2} ZN_AH_{AA} + \frac{1}{2} ZN_BH_{BB} + P_{AB}[\,H_{AB} - \frac{1}{2}\,(\,H_{AA} + H_{BB})] \tag{7.97}$$

Again enthalpy of mixture is

$$\Delta\mathrm{H}^{\mathrm{m}} = [\mathrm{H} - (\text{Enthaply of } \mathrm{N_A} \text{ atoms in pure A} + \text{Enthaply of } \mathrm{N_B} \text{ atoms in pure B })]$$
(7.98)

$$\Rightarrow \Delta H^m = P_{AB}[\,H_{AB} - \frac{1}{2}\,(H_{AA} + H_{BB}) \tag{7.99}$$

7.6.1 Application to Ideal & Regular Solutions:

Since $\Delta\mathrm{H}^{\mathrm{m}} = 0$ for ideal solution. So from equation (7.99), we will have

$$H_{AB} = \frac{1}{2}\,(H_{AA} + H_{BB}) \tag{7.100}$$

If N_0 is the total number of atoms in a solution. Then

$$x_A = \frac{N_A}{N_0}\ , x_B = \frac{N_B}{N_0} \tag{7.101}$$

[Where $N_0$is the Avogadro's number.]

Again total number of bonds is $\frac{1}{2}\,ZN_0$ in 1 mole. Hence we have

$$P_{AB} = 2\,x_Ax_B\,\frac{1}{2}\,ZN_0 = Z\,N_0x_Ax_B \tag{7.102}$$

[Where x_A & x_B are respective atoms]

Putting the equation (7.102) in equation (7.99), we have

$$\Delta \mathrm{H}^{\mathrm{m}} = Z\, N_0 x_A x_B\ [\, H_{AB} - \tfrac{1}{2}\ (H_{AA} + H_{BB}) \qquad (7.103)$$

Again we know

$$\Delta \mathrm{H}^{\mathrm{m}} = \mathrm{x_A x_B} \Omega \qquad (7.104)$$

Comparing above equation (7.103) and (7.104), we will have

$$\Omega = Z\, N_0\ [\, H_{AB} - \tfrac{1}{2}\ (H_{AA} + H_{BB})] \qquad (7.105)$$

7.6.2 <u>Application to non-regular solutions:</u>

In this case,

$$P_{AB} = Z\, N_0 x_A x_B \left\{1 - x_A x_B [\exp\left({}^{2\Omega}/_{ZRT}\right) - 1 \right\} \qquad (7.106)$$

Expanding the exponential & ignoring higher order terms, we will get

$$\Delta H^m \cong x_A x_B \Omega \left[1 - \left({}^{2\, x_A x_B}/_{ZRT}\right)\right] \qquad (7.107)$$

$$S^{xs} \cong -\left({}^{x_A^2\, x_B^2 \Omega^2}/_{ZRT^2}\right) \qquad (7.108)$$

$$G^{xs} \cong x_A\, x_B \Omega \left[1 - \left({}^{x_A x_B \Omega}/_{ZRT}\right)\right] \qquad (7.109)$$

7.7 <u>SIEVERT'S LAW:</u>

Statement of the law is "The atomic gases do not dissolve into the metal in their molecular form rather they dissolve by dissociation i.e. in atomic form."

So dissolution of a diatomic gas into metal (condensed phase)

Reaction 7.1: $x_2 \rightarrow 2x$ (In solution)

[Where $x_2 \rightarrow$ diatomic gases]

Equilibrium constant of reaction

$$K_p = \left[\frac{h_x}{[P_{x_2}]^{\frac{1}{2}}}\right]_{eq} \qquad (7.110)$$

[Where,

$h_x \rightarrow$ Henry activity of component x dissolve in condensed / solid phase.

$P_{x_2} \rightarrow$ Partial pressure of x_2.

$K_p \rightarrow$ Sievert's constant]

As the solubility of gases in condensed phase under moderate condition of temperature and pressure is very small. So, the h_x for the above expression for gases are preferred to use in terms of wt. %. The above equation (7.110) changes to

$$K_p = \frac{f_x\,(wt.\%\,x)}{P_{x_2}^{1/2}} \tag{7.111}$$

[Where

f_x → Henry's activity co-efficient]

In Henry's law if the activity co-efficient $f_x \rightarrow 1$, then equation (7.111) becomes

$$K_p = \frac{(wt.\%\,x)}{P_{x_2}^{1/2}} \tag{7.112}$$

$$\Rightarrow wt.\%\,x = K_p\sqrt{P_{x_2}} \tag{7.113}$$

$$\Rightarrow \mathrm{wt.\%\,x} = (\mathrm{Sievert'slaw\ constant}) \times \sqrt{\mathrm{P_{x_2}}} \tag{7.114}$$

From equation (7.113), Sievert's law can be expressed as, at constant temperature, the solubility of diatomic gases into the condensed phase is proportional to the square root of partial pressure.

7.7.1 Limitation of Sievert's Law:

It is applicable only to the limiting type of solution where Henerian activity $h_x \rightarrow 1$ (when ($f_x \neq 1$)) in such case expression for Sievert's law take the form

$$\ln(\mathrm{wt.\%\,x}) = \ln \mathrm{K_p} + \frac{1}{2}\ln \mathrm{P_{x_2}} - \ln \mathrm{f_x} \tag{7.115}$$

[Since, $f_x(wt.\%\,x) = (K_P)\left(P_{x_2}^{1/2}\right)$]

The function f_x can be expressed in terms of interaction co-efficient that means

$$\ln \mathrm{f_x} = \left(\epsilon_X^X.\mathrm{wt\%\,x}\right) + \left(\epsilon_X^1.\mathrm{wt\%\ of\ 1st\ component}\right) + \left(\epsilon_X^2.\mathrm{wt\%\ of\ 2nd\ component}\right) + \cdots + \left(\epsilon_X^n.\mathrm{wt\%\ of\ nth\ component}\right) \tag{7.116}$$

[Where,

ϵ_X^X −Self interaction parameter of the gas component "X"

$\epsilon_X^1, \epsilon_X^2, \ldots, \epsilon_X^n$ −Interaction parameter on component X of component 1, 2,..., n]

Problem-7.1: Calculate the solubility of N_2 gas under 1 atom pressure & 1600 ^{0}C in an iron-based alloyed having the composition C = 3.5%, Mn = 1%, Si = 1.2%, P = 0.5%. The interaction parameters for various components are

$$\epsilon_N^C = 0.25 \times 2.3 \text{ , } \epsilon_N^P = 0.51 \times 2.3, \epsilon_N^{Mn} 0.02 \times 2.3$$

$$\epsilon_N^N = 0, \epsilon_N^{Si} = 0.047 \times 2.3$$

Sievert's constant for N_2 (K_P) = 0.045

Solution:

As we from limiting condition of Sievert's law

$$\ln f_x = \left(\epsilon_N^C . \text{wt\% of C}\right) + \left(\epsilon_N^P . \text{wt\% of P}\right) + \left(\epsilon_N^{Mn} . \text{wt\% of Mn}\right) + \cdots + \left(\epsilon_N^N . \text{wt\% of N}\right)$$

$$= [(0.25 \times 3.5) + (0.51 \times 0.5) + (0.02 \times 1) + (0.047 \times 1.2)] \times 2.3$$

[Since, $\epsilon_N^N = 0$]

$$= [1.2064] \times 2.3 = 2.77472 \cong 2.775$$

Since, we know from Sievert's law as

$$f_x \times (wt.\%\, N) = Sivert' sconstant\ (K_P) \times \sqrt{P_{N_2}}$$

$$\Rightarrow wt.\%\, N = \frac{0.045 \times \sqrt{1}}{16.04} = (2.8 \times 10^{-3}) \qquad \text{(Ans)}$$

7.8 ONE WEIGHT PERCENT STANDARD STATE:

Raoult's law serves as references & Raoultian standard state used as conventional standard state where standard state of pure solid or pure liquid. Chipman proposed the "1 wt% of standard state" that can be used in various industrial purposes such in extraction & refining of liquid metals. Its features are

i. Composition scale is in wt%, not in mole fraction
ii. Henry's law rather that Raoult's law is the basis
iii. Answer for equilibrium calculations would be directly in wt%

Let in a multi-component solution using 1, 2, 3… i, j, … as components. Then conversion of wt.% into mole fraction can be done with the help of following equation as

$$X_i = \frac{{}^{W_i}/_{M_i}}{\Sigma\left({}^{W_i}/_{M_i}\right)} \qquad (7.117)$$

(Expression of mole fraction in terms of wt %)

[Where,

W_i - Wt % of i.

M_i → Molecular mass of i]

The reverse conversion follows

$$\Rightarrow W_i = \frac{100\, x_i M_i}{\sum x_i M_i} \tag{7.118}$$

7.8.1 <u>Definition & Relations for 1 wt% Standard State:</u>

Consider a dilute binary A-B solution where A is the solvent & B is solute then the activity of B in 1 wt% standard state is defined as

$$h_B = \frac{a_B}{\left({a_B}/{W_B}\right)_{W_B \to 0}} \tag{7.119}$$

[Where,

h_B → Activity of B in the new standard state.

a_B → Activity of B.

W_B → Wt% of B.]

When, $W_B \to 0$ Henry's law is obeyed. Hence $\left({a_B}/{W_B}\right)_{W_B \to 0}$ is constant. So, equation (7.119) becomes

$$h_B = \frac{a_B}{\left({a_B}/{W_B}\right)} = W_B \text{ , At } W_B \to 0 \tag{7.120}$$

In other words, the Henry's line (HL) $h_B = W_B$.

Now, consider the point on the Henry's line at $W_B = 1$, then using equation (7.120) h_B is also equal to 1. This is the 1 wt. % standard state.

Again standard states (SS) are either hypothetical or real. In real SS (Standard state) HL extends beyond $W_B = 1$ where hypothetically SS (Standard state), HL ends at $W_B = 1$. Follow the Fig-7.3 for more details.

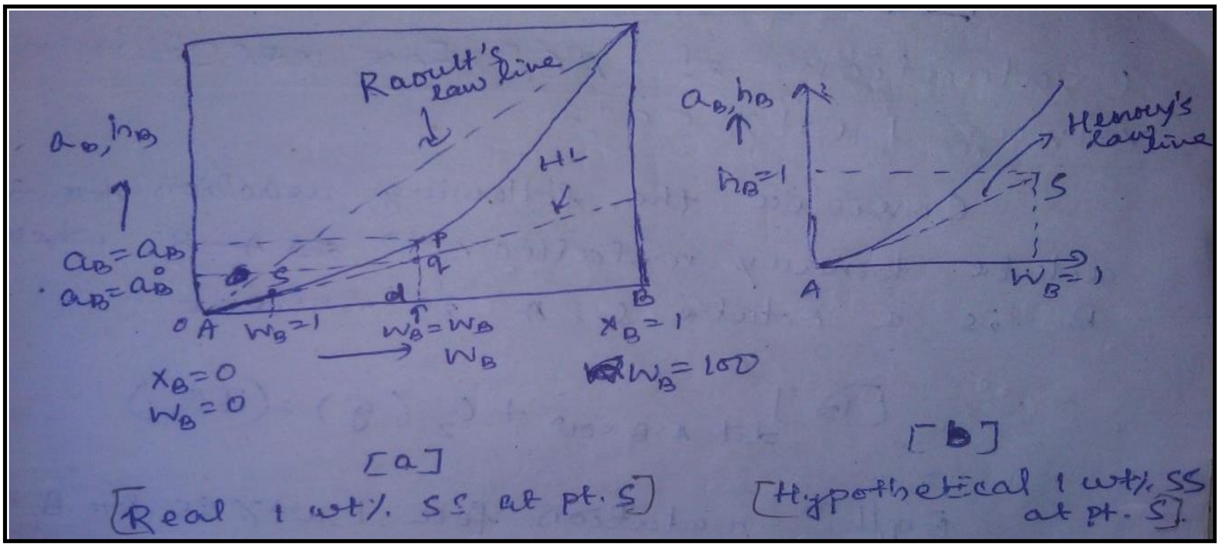

Fig 7.2: Graph (a) & (b) are showing real & hypothetical 1wt% SS at point S respectively.

From the figure 7.2, we have

At $W_B = W_B$, $Pd = h_B$, $qd = W_B$ for 1 wt % of SS. Hence,

$$\frac{Pd}{qd} = \frac{h_B}{W_B} = f_B = \text{Activity co-efficient of in wt \% of SS} \tag{7.121}$$

$$\text{At pt q, } a_B = a_B^0 = \gamma_B^0 x_B \tag{7.122}$$

$$\text{At pt P, } a_B = \gamma_B x_B \tag{7.123}$$

So, by considering the above equation (7.121) to (7.123), we have got

$$f_B = \frac{h_B}{W_B} = \frac{Pd}{qd} = \frac{a_B}{a_B^0} = \frac{\gamma_B x_B}{\gamma_B^0 x_B} = \frac{\gamma_B}{\gamma_B^0} \tag{7.124}$$

From equation (7.124), we have

$$\frac{h_B}{a_B} = \frac{W_B}{a_B^0} = \frac{W_B}{\gamma_B^0 x_B} \tag{7.125}$$

For binary A-B & $W_B = 0$, $W_A \to 100$ equation (7.117) gets simplified into

$$x_B = \frac{W_B/M_B}{W_A/M_A} = \frac{W_B/M_B}{100\,/M_A} = \frac{W_B\,M_A}{100\,M_B} \tag{7.126}$$

So using x_B value in equation (7.125), we have

$$\frac{h_B}{a_B} = \frac{100\,M_B}{\gamma_B^0 M_A} \tag{7.127}$$

7.8.2 Evolution of ΔG^0 for reaction involving 1 wt% SS:

Let us consider the reaction (7.2), for a dilute binary metallic solution A-B, where B is a solute & A is solvent.

Reaction-7.2: $[B]_{dil.A-B\ soln} + (O_2) = (BO_2)$

Then, equilibrium relation for 1wt% SS for B is given by

$$\Delta G_h^0 = -RT\ln K \tag{7.128}$$

$$\Rightarrow \Delta G_h^0 = -RT\ln\left[\frac{(a_{BO_2})}{(h_B)P_{O_2}}\right]_{\text{equ.}} \tag{7.129}$$

[Where,

ΔG_h^0, K_h are ΔG^0& K for 1 wt% SS for component B

"h" subscript denotes reference Henerian Line]

Corresponding equation in Raoultian SS are

$$\Delta G^0 = -RT\ln K = -RT\ln\left\{\frac{(BO_2)}{[a_B][P_{O_2}]}\right\}_{eqlm} \tag{7.130}$$

From equation (7.129) & (7.130), we have

$$\Delta G_h^0 - \Delta G^0 = -RT\ln\left(\frac{K_h}{K}\right) = -RT\ln\left(\frac{a_B}{h_B}\right) = RT\ln\left(\frac{h_B}{a_B}\right) \tag{7.131}$$

Combining this equation (7.131) with previous equation (7.127), we got

$$\Delta G_h^0 - \Delta G^0 = RT\ln\left(\frac{100\,M_B}{\gamma_B^0 M_A}\right) \tag{7.132}$$

$$\Rightarrow \Delta G_h^0 = \Delta G^0 + RT\ln\left(\frac{100\,M_B}{\gamma_B^0 M_A}\right) \tag{7.133}$$

Where,

- γ_B^0 depends on both B & A.
- Important solvents are liquid Fe, Cu, Pb, for these 1wt% measurement.

7.9 CHEMICAL POTENTIAL:

Thermodynamic equilibrium requires attainment of physic-chemical equilibrium, besides mechanical & thermal equilibrium. This means chemical potential should be uniform in the entire system in addition to uniformity of pressure & temperature.

There is a difference between the molar quantity (Q) & the same for system as whole (Q') as

$$Q' = n_T\,Q \tag{7.134}$$

[Where,

$n_T = Total\ number\ of\ moles = n_1 + n_2 + \ldots\ldots\ldots + n_i$]

By adopting the convention, let us consider a system with variable composition. Then the auxiliary relation becomes

$$dU' = TdS' - PdV' + \left(\frac{\delta U'}{\delta n_1}\right)_{S',V',n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\delta U'}{\delta n_i}\right)_{S',V',n_1,..,except n_i} dn_i \quad (7.135)$$

$$\Rightarrow dU' = TdS' - PdV' + \sum_i \left(\frac{\delta U'}{\delta n_i}\right) dn_i \quad (7.136)$$

$$\Rightarrow dU' = TdS' - PdV' + \sum_i \mu_i \, dn_i \quad (7.137)$$

[Where,

μ_i = Chemical potential for ith component for equation (7.137)

$= \left(\frac{\delta U'}{\delta n_i}\right)$ s’,v’, n$_1$, except n$_i$]

Similarly, we have

$$dH' = TdS' + VdP' + \left(\frac{\delta H'}{\delta n_1}\right)_{S',P',n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\delta H'}{\delta n_i}\right)_{S',P',n_1,..,except n_i} dn_i \quad (7.138)$$

$$\Rightarrow dH' = TdS' + VdP' + \sum_i \mu_i \, dn_i \quad (7.139)$$

$$dA' = -S'dT - PdV' + \left(\frac{\delta A'}{\delta n_1}\right)_{T',V',n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\delta A'}{\delta n_i}\right)_{T',V',n_1,..,except n_i} dn_i \quad (7.140)$$

$$\Rightarrow dA' = -S'dT - PdV' + \sum_i \mu_i \, dn_i \quad (7.141)$$

$$dG' = -S'dT + V'dP + \left(\frac{\delta G'}{\delta n_1}\right)_{T,P,n_2,..,except n_1} dn_1 + \cdots + \left(\frac{\delta G'}{\delta n_i}\right)_{T,P,n_1,..,except n_i} dn_i \quad (7.142)$$

$$\Rightarrow dG' = -S'dT + V'dP + \sum_i \mu_i \, dn_i \quad (7.143)$$

So, chemical potential for equation (7.139), (7.141) & (7.143) respectively are

$$\mu_i = \left(\frac{\delta H'}{\delta n_i}\right)_{S',P',n_1,..,except n_i} \quad (7.144)$$

$$\mu_i = \left(\frac{\delta A'}{\delta n_i}\right)_{T',V',n_1,..,except n_i} \quad (7.145)$$

$$\mu_i = \left(\frac{\delta G'}{\delta n_i}\right)_{T,P,n_1,..,except n_i} \quad (7.146)$$

So, μ_i is same as the partial molar extensive properties of component i in a solution.

7.9.1 Application of Chemical Potential:

i. Studies of phase equilibria

ii. In multi-component system, if we are interested in one component only. Then easily can be obtained by considering the chemical potential of that component.

iii. Allows easily visualization as to which way a species (element or compound) would tend to get transferred

7.9.2 Chemical Potential & activity:

Since, we know

$$\overline{G_i^m} = \overline{G_i} - G_i^0 = RT \ln a_i \qquad (7.147)$$

So, equation (7.147) may be rewritten in terms of chemical potential as

$$\mu_i^m = \mu_i - \mu_i^0 = RT \ln a_i \qquad (7.148)$$

So, at standard state accordingly to universal convention μ_i^0 is taken as Zero for all phases in the system. Therefore equation (7.148) becomes

$$\mu_i = RT \ln a_i \qquad (7.149)$$

Example:

Chemical potential of O_2 i.e. oxygen potential in both gas & liquid Cu co-existing at equilibrium may be written as

$$\mu_{O_2} = RT \ln a_{O_2} = RT \ln P_{O_2} \qquad (7.150)$$

[Where,

P_{O_2} → Partial pressure O_2 in gas at equilibrium.]

At equilibrium we can conclude

$$\boxed{\begin{array}{l} a_1^I = a_1^{II} \ldots\ldots\ldots\ldots = a_1^P \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ a_i^I = a_i^{II} \ldots\ldots\ldots\ldots = a_i^P \end{array}} \qquad (7.151)$$

[Where,

1, 2,……,i are components

I, II, ….. ,P are phases.]

N.B: Species i will be transferred from phase I to phase II, if $a_i^I > a_i^{II}$.

7.10 FREE ENERGY COMPOSITION DIAGRAM FOR BINARY ALLOYS SYSTEMS:

The free energy of each of phase's presents on a phase diagram can be plotted as a function of composition at a series of temperature. The phases co-exist in equilibrium are those correspond to the lowest free energy of the system.

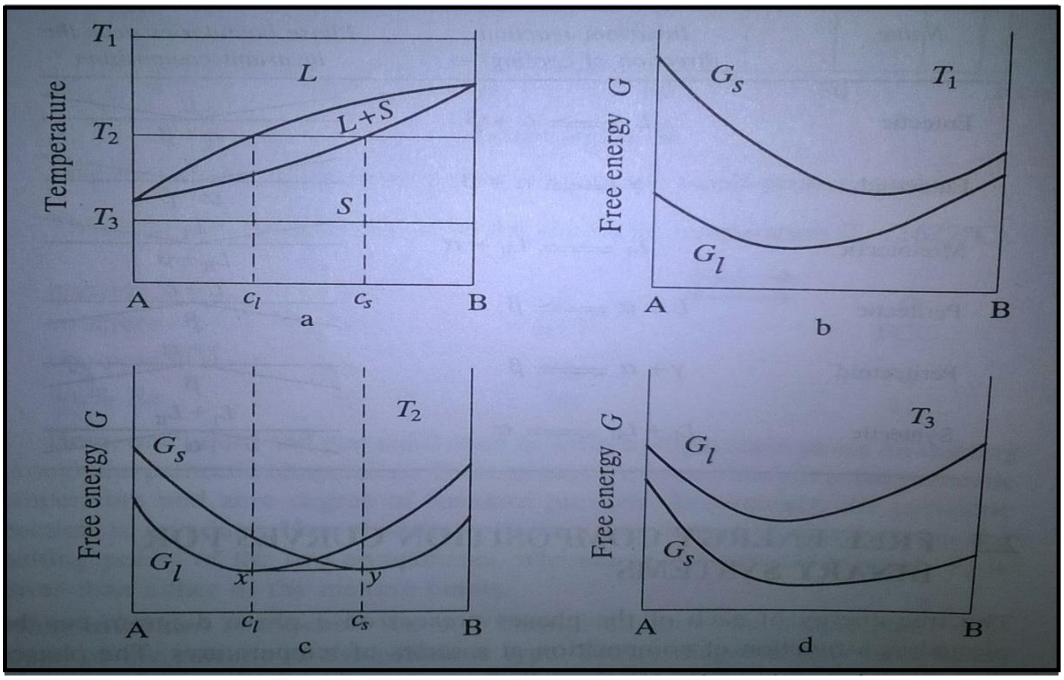

Fig 7.3: Free energy – composition relationships for an isomorphous system at three temperatures.

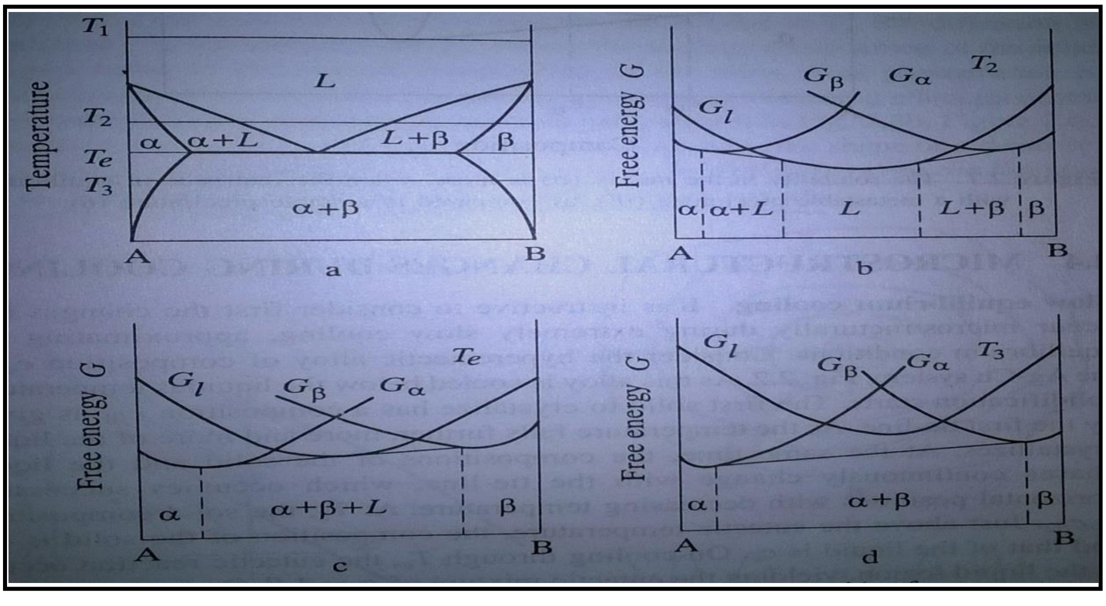

Fig 7.4: Free energy vs. composition relationships for a simple eutectic system at different temperature.

7.10.1 Binary Phase Diagram:

The most commonly used phase diagrams are those that depict the equilibrium between two components. These are known as binary phase diagrams.

Example: (Fe-Fe3C) phase diagram, (Cu – Ni) phase diagram.

For graphical representation of the binary phase prelateships, we need a map with three axes corresponding to temperature, pressure & composition. For binary phase diagrams, we ignore the pressure variable & the vapor phase.

As one of the variables has been arbitrarily omitted the phase rule for condensed phases (i.e. liquid & solids) only is written as

$$F = C - P + 1 \qquad (7.152)$$

7.10.1.1 Isomorphous system:

An Isomorphous system defined as the simplest binary phase diagram for a system that exhibiting complete liquid as well as solubility.

Example: Cu – Ni phase diagram

M. pt of Cu → 1083 ^{0}C

M. pt of Ni → 1455 ^{0}C

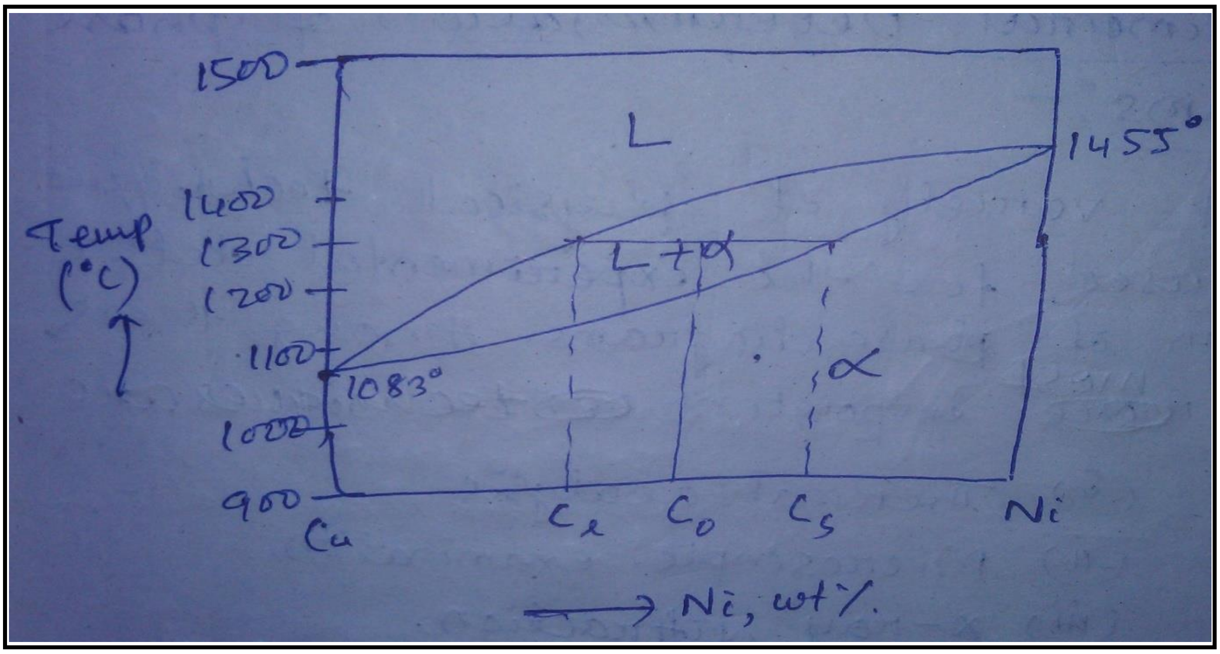

Fig 7.5: The Copper-Nickel phase diagram, showing complete solubility both in the liquid and in the solid states.

i. The liquid & solid regions are separated by a two-phase region, where both the phase co-exists.
ii. The boundary between two-phase region & the liquid is called liquidous line. The boundary between the two-phase region & the solid is called solidus line.
iii. **Solvus Line:** It is the solid-state phase boundary between the terminal solid solution & the two-phase region.

7.11 EXPERIMENTAL DETERMINATION OF PHASE DIAGRAMS:

A variety of physical techniques are used for the experimental determination of phase diagrams. Among these the most important techniques are

i. Thermal analysis.
ii. Microscopic examination.
iii. X-ray diffraction.

7.11.1 Determination of Liquidus and Solidus:

- Thermal analysis is the most important method for determination of the liquid-solid transformations
- This method based on evolution or absorption of heat occurs during a phase change
- When the temperature of an alloy sample is plotted as a function of time during heating or cooling, abrupt changes in slope of plot occur at points corresponding to the start or finish of a phase change

7.11.1.1 Cooling Curves:

Curves of single composition for different conditions using thermal analysis explained below.

Case – I: [For pure metal without super cooling]

- In this case, evolution of latent heat due to start of solidification is equal to heat loss due to surroundings. Follows fig 7.6 (a).
- Example: Pure metals like Fe, Cu, Ni etc.

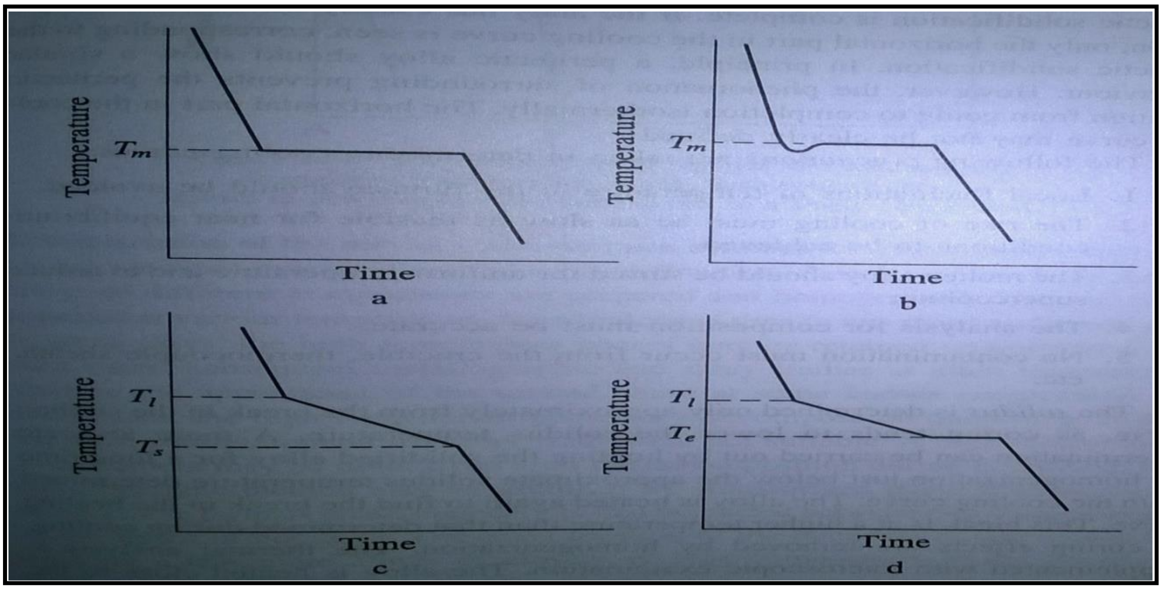

Fig 7.6: Thermal analysis. Cooling curves (a) for a pure metal without supercooling, (b) for a pure metal with supercooling, (c) for a solid solution alloy, (d) for a hypoeutectic alloy.

Case – II: [For a pure metal with super-cooling]

- In this case, evolution of latent heat due to the solidification less than heat lost to the surroundings and this process is known as Super-cooling. Follows fig 7.6 (b).
- Once Solidification starts heat evolution raise the sample temperature back to freezing point.

Case – III: [For a solid solution alloys]

- From fig 7.6 (c) we have, first arrest indicating abrupt decrease in the cooling rate occurs as the liquidus temperature T_l is crossed. Since, over a range of temperature the solidification occurs. So there is no horizontal part.
- The second arrest is observed at the solidus temperature T_s, when the cooling rate starts to increase again.

Case – IV: [For a hypothetical alloy or pro-eutectic binary alloy]

- From fig 7.6 (d) we have, Peritectic alloy also shows the similar behavior as pro-eutectic or hyper-eutectic alloy.
- First arrest occurs at the liquidus temperature & the cooling rate decreases.

- At the eutectic temperatureT_e, the cooling curve becomes horizontal as invariant eutectic reaction occurs isothermally. The cooling rate increases again when the eutectic solidification is complete.

Following precautions are taken to determining cooling curves

i. Local fluctuations of temperature in the furnace should be avoided.
ii. For the achievement of near equilibrium conditions, the rate of cooling must be slow as feasible.
iii. To reduce super cooling, the molten alloy should be stirred for uniform temperature.
iv. Composition analysis must be accurate.
v. No contamination must occur from the crucible, thermocouple sheath etc.

Solidus is determined by approximate lines in cooling curve, as coring tends to lower the solidus temperature. A more accurate determination can be carried out by holding the solidified alloy for a long time for homogenization just below the approximate solidus temperature determined from cooling curve. The alloy heated again to find the breaking in the heating curve. This break is at a higher temp then that determined during cooling as coring effects are removed by homogenization.

Coring: above solidus temperature same liquid remains without transfer to solid is known as coring.

Thermal analysis can be replaced with microscopic examination; the alloy is heated close to the solidus & quenched to ascertain microscopically the appearance of the first chilled liquid.

Using the break in the cooling & heating curves for a series of compositions covering the entire binary range, the liquidus & solidus boundaries can be fully determined.

7.11.2 Determination of the Solvus:

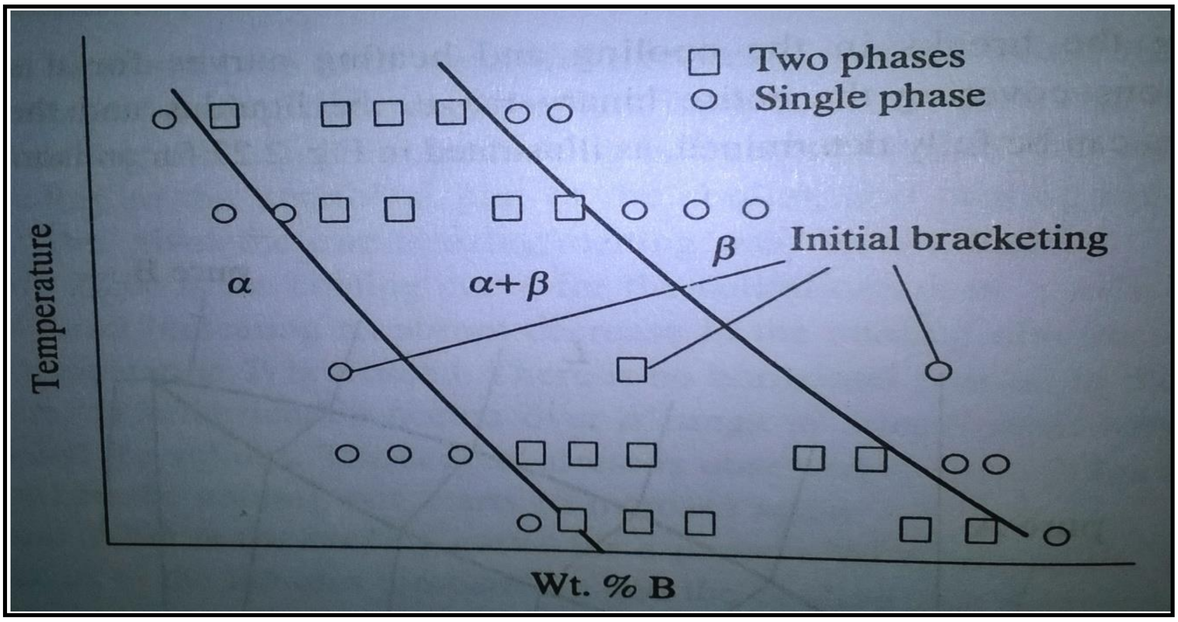

Fig 7.7: Determination of Solvus boundaries by the metallographic & X-ray methods.

The common methods for determining the Solvus are microscopic examination & X-ray diffraction. A series of small ingots of alloys of different compositions are prepared and homogenized. They are then annealed at various temperatures for prolonged time (a few days) and quenched.

In such cases, subsequent metallographic and X-ray studies at room temperature disclose the appearance of second phase at some known composition.

In other cases, at high temperature phase may decompose on quenching, If this happens room temperature, X-ray studies are not suitable. So a high temperature X-ray camera used.

But even after the decomposition during quenching the metallographic method may be useful, if the transformed phase is in an easily recognizable form.

A phase boundary is first bracketed between two compositions and then exact location of boundary is determined by studying a few more alloys of closely varying composition in the boundary region.

7.12 CLAPEYRON EQUATION:

Consider a phase transformation of an element or compound (designated as A)

Reaction 7.3: A (phase I) = A (phase II)

For phase I: $dG_A(I) = V_A(I)dP - S_A(I)dT$ (7.153)

For phase II: $dG_A(II) = V_A(II)dP - S_A(II)dT$ (7.154)

At equilibrium phase transformation temp (T_{tr}) and pressure (P_{tr})

$$\Delta G = G_A(II) - G_A(I) = 0 \tag{7.155}$$

$$\Rightarrow G_A(II) = G_A(I) \tag{7.156}$$

$$\Rightarrow dG_A(II) = dG_A(I) \tag{7.157}$$

So, due change the system have achieved new state of equilibrium where pressure is $P_{tr} + dP$, temp is $T_{tr} + dT$ and also Gibb's free energy change to $G_A(I) \rightarrow G_A(I) + dG_A\,(I)$ & $G_A(II) \rightarrow G_A(II) + dG_A\,(II)$.

So, summarizing all the things we have got

Initial condition **(Up to phase transformation)**	**Final condition** **(After phase transformation)**
1. Temperature T_{tr}	1. $T_{tr} + dT$
2. Pressure P_{tr}	2. $P_{tr} + dP$
3. Gibb's free energy $G_A(I)$& $G_A(II)$ $\Delta G = G_A(II) - G_A(I)$	3. Gibb's free energy (at eqlb^{m}) $G_A(I) \rightarrow G_A(I) + dG_A\,(I)$ $G_A(II) \rightarrow G_A(II) + dG_A\,(II)$ $\Delta G = \left(G_A(II) + dG_A\,(II)\right) - (G_A(I) + dG_A\,(I))$
4. Volume $V_A(I)$ & $V_A(II)$	4. Volume $V_A(I) + dV_A(I)$, $V_A(II) + dV_A(II)$
5. Entropy $S_A(I)$ & $S_A(II)$	5. Entropy $S_A(I) + dS_A(I)$, $S_A(II) + dS_A(II)$

From equation (7.157), we got

$$V_A(I)dP - S_A(I)\,dT = V_A(II)dP - S_A(II)\,dT \tag{7.158}$$

$$\Rightarrow [S_A(II) - S_A(I)]\,dT = [V_A(II) - V_A(I)]dP \tag{7.159}$$

$$\Rightarrow \left(\frac{dT}{dP}\right)_{eqlbm} = \frac{V_A(II) - V_A(I)}{S_A(II) - S_A(I)} \tag{7.160}$$

$$\Rightarrow \left(\frac{dT}{dP}\right)_{eqlbm} = \frac{\Delta V_{tr}}{\Delta S_{tr}} \tag{7.161}$$

Since, we know

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}} \tag{7.162}$$

So, equation (7.161) becomes

$$\left(\frac{dT}{dP}\right)_{eqlbm} = \frac{\Delta V_{tr}\,T_{tr}}{\Delta H_{tr}} \tag{7.163}$$

The equation (7.163) is known as **Clapeyron equation**

CHAPTER-8

TOPOCHEMICAL REACTION

8.1 TOPOCHEMICAL REACTION:

It is defined as the solid-gas reaction or phase boundary controlled reactions that occur by the movement of well-defined interface.

Diffusion steps:

i. Diffusion of reduce gas (CO, H_2) from gas phase to the ore-pellet through surface film.
ii. Diffusion of reduce gas from ore-pellet to reductant layers.
iii. Chemical reaction carry out as

Reaction 8.1: $[M_xO_y + \ YCO \ \rightarrow XM + YCO_2]$

Reaction 8.2: $[M_xO_y + \ H_2 \ \rightarrow XM + YHO_2]$

iv. Diffusion of product gas (CO_2, H_2O) from reductant layer to ore-pellet
v. Diffusion of product gas from ore-pellet to surface film.

Fig 8.1 represents a schematic diagram of Gaseous reduction of iron ore, where reduction occurs by using CO gas.

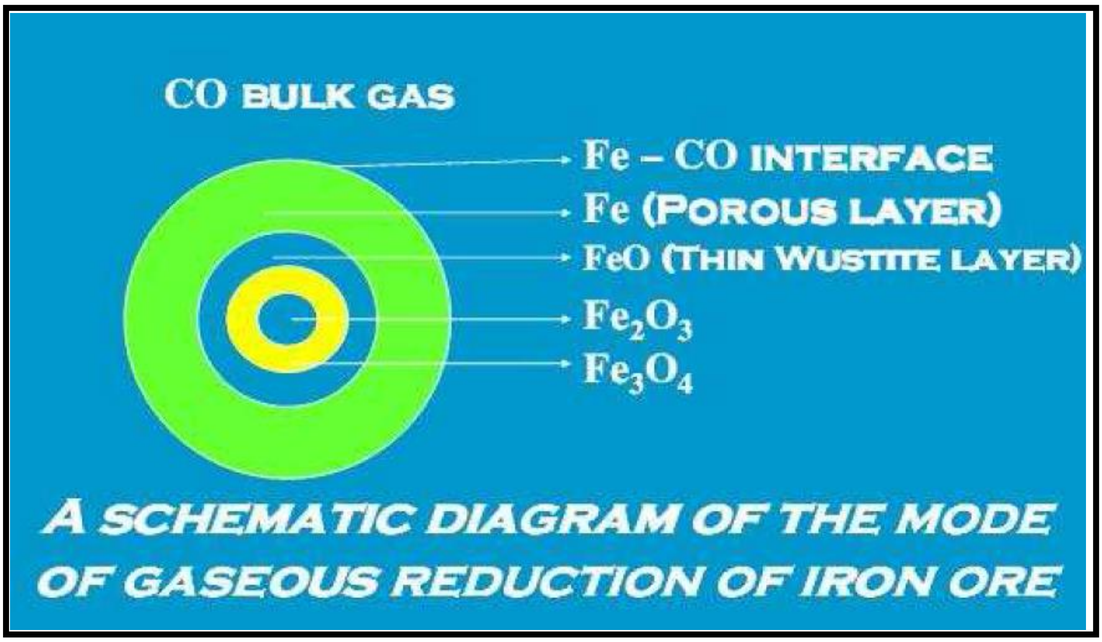

Fig. 8.1: Reduction of iron ore presence of CO gas

8.1.1 Derivation:

Let us assume the particle which is participating in reduction reaction are spherical in nature for which the reaction is phase boundary type, then the presence or absence of product layer the rate of reaction depends on the interface area.

$$-\frac{dw}{dt} \propto A.C \;\Rightarrow\; -\frac{dw}{dt} = KAC \tag{8.1}$$

Negative sign indicates that with increase in time the wt. decreases

[Where,

K → Reaction constant

A → Interface area for chemical reaction

C → Concentration of the reagent fluid.]

If "r" be the radius of the spherical molecules, participating in the equation (8.1) can be re-written as

$$-\frac{d}{dt}\left[\frac{4}{3}\pi r^3.\rho\right] = K.4\pi r^2.1 \tag{8.2}$$

[Where, $A = 4\pi r^2$, C=1]

Reaction not started so, C = 1, for unreacted core sphere.

$$\Rightarrow -\frac{dr}{dt} = \frac{3K}{\rho} \tag{8.3}$$

$$\Rightarrow -\frac{dr}{dt} = \frac{K'}{\rho} \tag{8.4}$$

$$\Rightarrow -\int_{r_0}^{r} dr = \frac{K'}{\rho}\int_0^t dt \tag{8.5}$$

$$\Rightarrow -(r - r_0) = \frac{K'}{\rho}\,t \tag{8.6}$$

$$\Rightarrow (r_0 - r) = \frac{K'}{\rho}\,t \tag{8.7}$$

Again,

$$\alpha = [\text{degree of reaction at } (t = t_0)] = \frac{W_0 - W}{W_0} = \frac{\text{Change in wt.}}{\text{Initial wt.}} \tag{8.8}$$

Since, the weight decreases with time. So, degree of reduction (α) expressed as

$$Degree\ ofreduction\ (\alpha) = \frac{\text{Initial wt.} - \text{Final wt.}}{\text{Initial wt.}} \tag{8.9}$$

$$\Rightarrow \alpha = \frac{W_0 - W}{W_0} = 1 - \frac{W}{W_0} = 1 - \left(\frac{{}^4/_3\pi r^3\rho}{{}^4/_3\pi r^3\rho}\right) = 1 - \left({}^{r}/_{r_0}\right)^3 \tag{8.10}$$

$$\Rightarrow \left(\frac{r}{r_0}\right)^3 = 1 - \alpha \tag{8.11}$$

$$\Rightarrow {}^{r}/_{r_0} = (1 - \alpha)^{1/3} \tag{8.12}$$

$$\Rightarrow r = r_0\,(1 - \alpha)^{1/3} \tag{8.13}$$

Replacing the in equation (8.13) in equation (8.7), we will get,

$$\Rightarrow \left[r_0 - r_0(1 - \alpha)^{1/3}\right] = \frac{K't}{\rho} \tag{8.14}$$

$$\Rightarrow r_0\left[1 - (1 - \alpha)^{1/3}\right] = \frac{K't}{\rho} \tag{8.15}$$

$$\Rightarrow r_0\left[1 - (1 - \alpha)^{1/3}\right] = \frac{K't}{\rho} \tag{8.16}$$

The above equation (8.16) is known as **Mckewan relation or model**

If we will take the experimental data and plot $\left[1 - (1 - \alpha)^{1/3}\right]$ vs t and getting a straight line, then we can say reduction reaction obeys Mckewan relation.

8.2 JOHNSON – MEHL'S EQUATION:

i. It is based on α vs t graph.

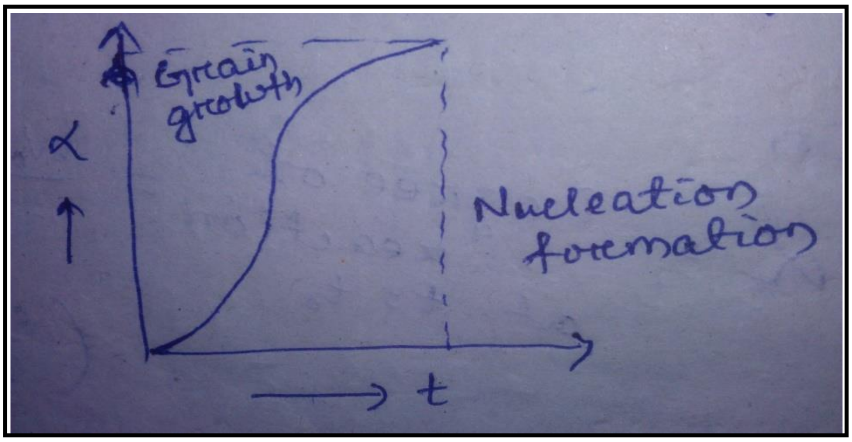

Fig 8.1: α vs t graph.

ii. Initially, rate of reaction(α) increase with time to a fixed extent with a faster rate. But, after maximum point the rate of reaction (α) increase with time with a slower rate.

iii. It is used to find out the dimension & order of reaction.

Relation between rate of reaction and time defined by the following equation (8.17),

$$\frac{d\alpha}{dt} = K^{n}\, t^{n-1}(1-\alpha) \tag{8.17}$$

$$\Rightarrow \int \frac{d\alpha}{1-\alpha} = K^{n} \int t^{n-1} dt \tag{8.18}$$

$$\Rightarrow -\ln(1-\alpha) = \frac{K^{n}t^{n}}{n} \tag{8.19}$$

$$\Rightarrow \ln(1-\alpha)^{-1} = \ln\left(\frac{1}{1-\alpha}\right) = \frac{K^{n}t^{n}}{n} \tag{8.20}$$

$$\Rightarrow \frac{1}{(1-\alpha)} = \exp\left(\frac{K^{n}t^{n}}{n}\right) \tag{8.21}$$

$$\Rightarrow \alpha = 1 - \left[{}^{1}\Big/_{\exp\left(\frac{K^{n}t^{n}}{n}\right)}\right] \tag{8.22}$$

<u>Or</u>

From equation (8.20), we can also write

$$\Rightarrow \log\left({}^{1}/_{1-\alpha}\right) = \frac{1}{2.303}\,(K^{'}t)^{n} \tag{8.23}$$

$$\left[\text{Where } K^{'} = {}^{K}\!/_{n^{1/n}}\right]$$

$$\Rightarrow \log\log\left({}^{1}/_{1-\alpha}\right) = n\log K^{'} + n\log t - \log(2.303) \tag{8.24}$$

$$\Rightarrow \int \frac{d\alpha}{1-\alpha} = K^{n} \int t^{n-1}\, dt \tag{8.25}$$

$$\Rightarrow \ln\left(\frac{1}{1-\alpha}\right) = \left(\frac{K^{'}}{n^{1/n}}\right)^{n} = (K^{'})^{n}\, t^{n} \tag{8.26}$$

$$\Rightarrow \log\left(\frac{1}{1-\alpha}\right) = \frac{(K^{'})^{n}\, t^{n^{n}}}{2.303} \tag{8.27}$$

$$\Rightarrow \log\log\left(\frac{1}{1-\alpha}\right) = n\log K^{'} + n\log t - \log 2.303 \tag{8.28}$$

8.3 TYPES OF REACTION:

There are basically two types of reactions existing. The differences between two reactions are given below

Homogeneous Reaction	**Heterogeneous Reaction**
- It takes place entirely within one phase where reactants and products both are in one phase as well as reaction carry out in that phase.	- It involves more than one phase. Example: slag-metal reaction; molten slag is in one phase and molten metal in another phase, reaction takes place at interface.
- Reaction occurs in the bulk i.e. within the phase.	- Reaction occurs not in bulk but at the interface.
- Rate of chemical reaction is proportional to the volume of the phase.	- Rate of chemical reaction to the interfacial area between the two or more phases
- No adsorption and desorption are involved in homogeneous reaction	- Heterogeneous reaction involves following steps (a) Absorption of reactants into the interfacial layer (b) Chemical reaction between absorbed components (c) Desorption of products into the phase.
- Reaction mechanism is not complex	- Reaction mechanism is complex.
- **Example:** Reaction between gas molecules to produce gaseous products	- **Example:** Transfer of a element or ion from molten slag to molten metal in a refining process.

Most of the metallurgical reactions are heterogeneous. The main types of heterogeneous reactions are discussed below:

(i) **Gas – Solid :** Reaction of oxide with $\left(\mathrm{CO}/_{\mathrm{H_2}}\right)$ gas oxidation of metal

Example:

a. $\mathrm{Fe_2O_2(s) + 3CO(g) \rightarrow 2Fe + 3CO_2}$

b. $\mathrm{2Fe + O_2 \rightarrow 2FeO}$

(ii) **Gas –Liquid:** Gaseous reduction in hydro-metallurgy.

(iii) **Liquid – Liquid:** Metal – slag reaction

(iv) **Liquid – Solid:** Leaching and corrosion reactions

Example:

a. Leaching of sulphide with liberation of elemental of S

$$\mathrm{CuS^{+} + 2Fe^{3+}\,(ferric) \rightarrow Cu^{2+} + S + 2\,Fe^{2+}(ferrous)}$$

b. Cementation process:

$$\mathrm{Cu^{2+}\,(cupric) + Fe \rightarrow Cu\,(metallic\ copper) + Fe^{2+}(ferrous)}$$

(v) **Solid – Solid:**

Example:

a. Reduction of ZnO with C **i.e.** $\mathrm{ZnO + C \rightarrow Zn + CO}$

b. Metallothermic reaction

$$\mathrm{Cr_2O_3 + 2Al \rightarrow Cr_2 + Al_2O_3}$$

8.3.1 Reaction of Flat Plate:

Let us consider a small plate of material having area and thickness d. For the first instant let's assume that any one of the surface has been exposed to a reacting gas. During the course of the reaction let's assume the thickness of the product produced is 'y' and with increase in time that thickness gets increased. If the diffusion of reacting gas through the product layer is the rate controlling. Then rate of the reaction is given as

$$Rate\ of\ reaction = \frac{dw}{dt} = \frac{D.A.C}{y} \tag{8.29}$$

[Where,

w – Weight of product after time t

D – Diffusion co-efficient

A – Area of the surface that available for reaction

C – Concentration]

Since

Weight (w) = volume × Density = (Area × Length) × Density

$$= A.\ y.\ \rho \tag{8.30}$$

Put equation (8.30) in equation (8.29), we have

$$\frac{d(A.y.\rho)}{dt} = \frac{D.A.C}{y} \tag{8.31}$$

$$\Rightarrow \frac{dy}{dt} = \left(\frac{D.C}{\rho}\right) \times \frac{1}{y} \tag{8.32}$$

Since $\frac{DC}{\rho} = constant = K$ (suppose), then equation (8.32) becomes

$$\frac{dy}{dt} = \frac{K}{y} \tag{8.33}$$

$$\Rightarrow \int ydy = K \int dt \tag{8.34}$$

$$\Rightarrow y^2 = Kt \tag{8.35}$$

The above equation (8.35) is known as **Parabolic law**.

8.4 REACTION IN LUMPS:

Steps followed during reaction in lump are given by

a. Diffusion of reductant gas CO/H_2 through boundary surface.
b. Diffusion of reductant gas CO/H_2 through macro pore.
c. Diffusion of reductant gas CO/H_2 through micro pore.
d. Diffusion of reductant gas CO/H_2 through product layer.

e. Reaction between CO/H_2 gas & Metal Oxide

$$\left[M_xO_y + \ YCO \ \rightarrow XM + YCO_2\right]$$

$$\left[M_xO_y + \ H_2 \ \rightarrow XM + YHO_2\right]$$

Example: $Fe_2O_3 + 3CO/H_2 = 2Fe + 3CO_2/H_2O(\uparrow)$

f. Diffusion of product gas CO_2/H_2O through product layer.

g. Diffusion of product gas CO_2/H_2O through micro pore.

h. Diffusion of product gas CO_2/H_2O through macro pore.

i. Diffusion of product gas CO_2/H_2O through boundary layer/surface.

8.5 IMPORTANT NOTES:

a. Reformed Natural Gas: It is defined as the gas that produces due to reaction between CH_4 with H_2O using N_2 catalyst.

$$CH_4 + H_2O \overset{N_2}{\leftrightarrow} CO + 3H_2$$

b. Degree of Reduction: It is defined as the ratio of amount of O_2 removed at any time (t) to that of total possible amount of removal oxygen.

$$Degree\ of\ reduction(\alpha) = \frac{Amount\ of\ O_2\ removed\ at\ time\ t}{Total\ possible\ O_2\ removal}$$

c. Metallization: It is defined as the ratio of metal Fe to that of total Fe present in Fe and its oxides.

$$Metallization = \frac{Metal\ Fe}{Total\ Fe}$$

$$Degree\ of\ Metallization = MEtallization \times 100$$

8.6 DIFFERENCE BETWEEN MOLECULARITY AND ORDER OF THE REACTION:

The difference between Order of reaction and Molecularity explained below

Sl. No.	Molecularity	Order of Reaction
1	It is the number of reacting species undergoing collisions the reactions.	It is the sum of the power of the conc. terms in the rate law expression.
2	It is a theoretic value.	It is determined experimentally
3	It has positive integral value 1, 2,3…n.	It can have negative & fractional value also.
4	It does not tell us anything about the mechanism of the reaction.	It tells us about some clue about mechanism of the reaction.
5	It does not change with change in temperature and pressure.	It may change with change in temperature and pressure.
6	It is the property of only elementary reactions and has no meaning for complex reactions.	It is the property of both elementary and complex reaction.

CHAPTER-9

ELECTROMETALLURGY

9.1 THERMODYNAMIC OF ELECTROCHEMICAL CELLS:

9.1.1 Laws of Electrolysis:

Electrolysis implies the processes which utilize electrical energy for extraction of metals (Example-Cu, Al, Zn etc) which known as **electro winning** and for purification of metals (Example-Cu, Al, Pb etc) which known as **electro refining**.

In case of electro winning, the anode is insoluble conductor while in electro refining, it is impure metal itself. The electrolyte in each case is a solution with sufficiently high electrical conductivity and solute concentration. The cathode may be pure metal or a blank of another metal.

Electrolytic dissociation of ionic media is governed by two laws, which are known as Faraday's laws of electrolysis.

9.1.1.1 Faraday's First Law:

It states that "The weight of material (W) deposited at an electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte".

Mathematically can be expressed as

$$W \,\alpha\, Q \;\Rightarrow W \,\alpha\, (I \times t) \quad [Since\; Q = I \times t] \tag{9.1}$$

$$\Rightarrow W = Z \times I \times t \tag{9.2}$$

[Where

I – Electric Current (in amp), t – Time (in sec.)

W – Weight deposited (in gm.), Z – Electrochemical Equivalent]

N. B.: Electrochemical Equivalent (Z): It is defined as the weight deposited by a current of 1 amp during its passage for duration of 1 sec.

9.1.1.2 Faraday's Second Law:

It states that "The weight of material (W) deposited at an electrode is directly proportional to the equivalent weight (E) of the material".

Mathematically can be expressed as

$$W \,\alpha\, E \;\Rightarrow E \,\alpha\, W \;\Rightarrow\; E = F \times W \tag{9.3}$$

$$\Rightarrow F = \frac{E}{W} = \frac{(A/Z)}{W} = \frac{A}{(Z \times W)} \qquad (9.4)$$

$$(Since\ E = \frac{Atomic\ wt.(A)}{Valency\ (Z)})$$

[Where,

F – Proportionality Constant known as Faraday's constant

$F \approx 96500$ Coulomb/gm. eq.

A – Atomic Mass, W – Weight deposited (in gm.)

Z – Valency, E – Equivalent weight]

Combined 1st and 2nd laws of Faraday, we have

$$W\ \alpha\ Q \times E\ \Rightarrow\ (Q \times E)\ \alpha\ W \qquad (9.5)$$

$$\Rightarrow Q \times E = F \times W \qquad (9.6)$$

Now putting $E = {}^{A}/_{Z}$ and $Q = (I \times t)$ in equation (9.6), we will get

$$I \times t = \frac{F \times W}{A/Z} \qquad (9.7)$$

$$\Rightarrow W = \frac{I \times t \times A}{F \times Z} \qquad (9.8)$$

9.1.2 Some Important Parameters in Electrometallurgy:

1. **Current Efficiency:** It is defined as the ratio of the actual mass of the substance (metal) liberated from an electrolyte by the passage of current to the mass of the substance liberated theoretically according to Faraday's law.

Mathematically it is represented as

$$Current\ Efficiency\ (\eta_I) = \frac{Theoretical\ amount\ of\ Electricity\ required}{Actual\ amount\ of\ Electricity\ consumed}$$

$$= \frac{Actual\ amount\ of\ metal\ deposited}{Theoretical\ amount\ of\ metal\ deposited} \tag{9.9}$$

2. **Electric Power:** It is defined as the ratio of electric power used per day with actual weight of metal deposited.

Mathematically it is represented as

$$Electric\ Power (in\ watts) = \frac{Electric\ power\ used\ per\ day}{Actual\ weight\ of\ metal\ deposited}$$

$$= \frac{(Voltage\ drop \times Current)}{Actual\ weight\ of\ the\ metal\ deposited} \tag{9.10}$$

9.1.3 Thermodynamics of Electrochemical Cells:

An Electrochemical reaction involves coupling of chemical reaction with the flow of Electric current.

- Many metals are extracted and refined by electrolytic process (Zn, Al, Mg etc.).
- Electroplating and anodizing are employed for surface protection of metals and alloys from corrosion.
- Electrochemical reactions occur in Corrosion, Hydrometallurgy and slag-metal reactions.
- Electrochemical method used for high temperature measurement tools.
- Batteries are Electrochemical cell.

Electrochemical cells are broadly classified into two categories

1. Galvanic Cells: In this case, stored chemical energy is converted into electrical energy.
2. Electrolytic Cells: In this case, stored electrical energy is used to do chemical work.

Thermodynamic studies/predictions/measurements can be done properly only for Galvanic cells. These are can be made to operate reversibly.

9.1.3.1 Daniel Cell:

Most common example of Galvanic cell is Daniel cell.

Reaction 9.1: Overall Reaction: $Zn(S) + CuSO_4(aq) = Cu(S) + ZnSO_4(aq)$

Reaction 9.2: Overall reaction (Ionic form): $Zn(S) + Cu^{+2}(aq) = Cu(S) + Zn^{+2}(aq)$

Reaction Consists of

Reaction 9.3: Anodic Reaction: $Zn(S) = Zn^{+2}(aq) + 2\bar{e}(Oxidation)$

Reaction 9.4: Cathodic Reaction: $Cu^{+2}(aq) + 2\bar{e} = Cu(S)(Reduction)$

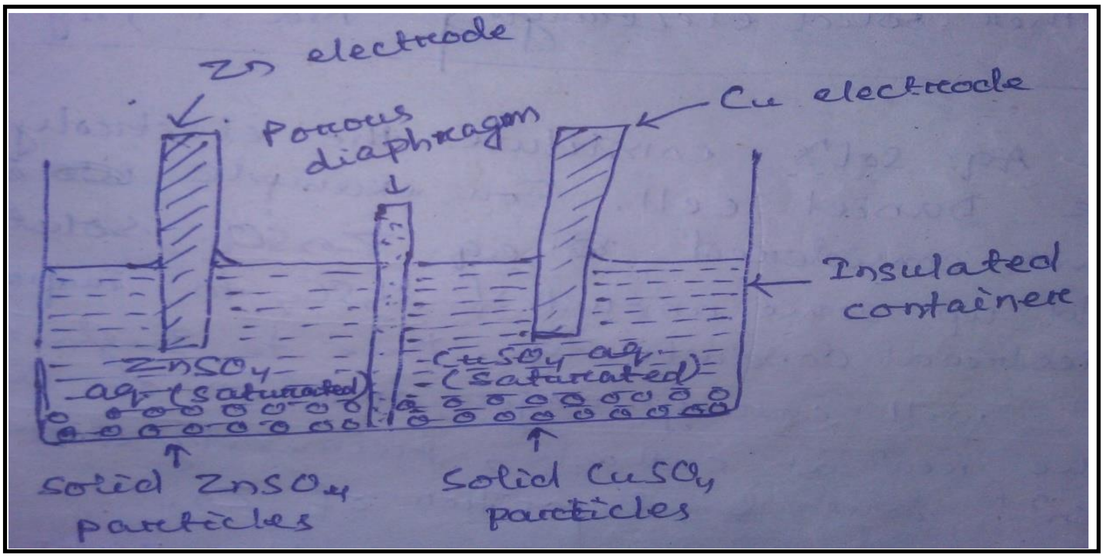

Fig 9.1: Schematic diagram of Daniel Cell

Electrolytes are ionic liquids or solids and classified as follows

Classification of Electrolytes

Sl. No.	**Electrolytes**	**Examples of current carrying Ions**
1	Aqueous Solutions	Na^+, H^+, Cl^- etc
2	Molten Salts	$Na^+, K^+, Cd^+, Cl^-, F^- etc$
3	Molten Slags	Ca^{+2}, Mn^{2+} etc
4	Solid Oxide Electrolytes	O^{2-}
5	Other Solid Electrolytes	Na^+, Ag^+, F^-, Li^+ etc

Aqueous solutions constitute the electrolytes in the Daniel cell. For example if we have considered aq. $ZnSO_4$ solution, then add up some amount of H_2SO_4 to improve its electrical conductivity. Due to high mobility H^+, it will carry major fraction of current. The reaction at cathode, primarily discharge of Zn^{2+} ions and deposition of Zn.

Similarly by taking molten salts at high temperature may consists of NaCl, KCl and $CdCl_2$. But only Cd^{2+} will participate in electrochemical reaction.

Generally, for aqueous solutions as electrolyte, the electrochemical cell operated at room temperature. For molten salts, it is about $(400\text{-}900)^0$C. For molten slag case, it is about $(1000\text{-}1500)^0$C.

9.1.3.2 Solid Electrolyte:

In case of solid electrolytes, the operated temperature generally very high and it depends upon the nature of electrolytes. Out of many, Zirconia (ZrO_2) is well known solid electrolyte. It is a high temperature ceramic material.

Zirconia is stable at high temperature but it undergoes some phase transformation during heating and cooling. Due to which there thermal stresses developed and that may be cause failure in service. To remove these chances, there are various oxides such as CaO, MgO and Y_2O_3 added and as a result melting point of ZrO_2 get increased to approximately 2400^0C.

Let us consider the example of ZrO_2-CaO solid solution. In pure ZrO_2, Zr^{4+} ions occupy cationic sites and O^{2-} ions occupy anionic sites. So after the addition of CaO to ZrO_2, some of Ca^{2+} replace the Zr^{2+} from the cationic sites and allows the movement of O^{2-} ions. Since Ca^{2+} and Zr^{4+} are almost immobile around above (700-800)^{0}C. Thus the cell operated at high temperature.

Besides ZrO_2-CaO solid electrolytes, other important solid electrolytes are ZrO_2-Y_2O_3, ThO_2-Y_2O_3, CaF_2 doped with YF_3 etc.

9.2 THERMODYNAMIC OF REVERSIBLE GALVANIC CELLS:

Some electrical cell can be made to behave either as a Galvanic cell or as an electrolytic cell.

Example: Daniel Cell.

If external DC source connected to the cell having imposed voltage (V_{ext}), that opposes that of the Daniel Cell voltage (V_{cell}). Then depending on magnitude of V_{ext} and V_{cell}, we have two conditions

Condition-1:

- $V_{ext} < V_{cell} \Rightarrow Cell\ behaves\ as\ Galvanic\ cell$
- Cell reaction is

Reaction 9.5: $Zn(S) + CuSO_4(aq) = ZnSO_4(aq) + Cu(S)$

Condition-2:

- $V_{ext} > V_{cell} \Rightarrow Cell\ behaves\ as\ elecrolytic\ cell$
- Cell reaction is

Reaction 9.6: $Cu(S) + ZnSO_4(aq) = CuSO_4(aq) + Zn(S)$

In an electrolytic cell, chemical reaction occurs only if current allowed to flow through the cell. But if no current flow i. e. circuit becomes open then at that time voltage is known as emf or electromotive force of the Galvanic cell.

Reversible Galvanic cell possible if and only

1. Use of a voltmeter of very high resistance makes current flow negligible.
2. Impose voltage from external source, $V_{ext} \cong V_{cell}$ i. e. emf of the cell and as a result current flow is negligible.

9.3 RELATION BETWEEN CELL EMF (E) AND FREE ENERGY OF CELL REACTION (ΔG):

From a reversible process

$$dG = VdP - SdT - \delta W' \tag{9.11}$$

[Where,

W' – Work done other than work done against pressure]

At constant P and T,

$$dG = -\delta W' \tag{9.12}$$

In case of a reversible Galvanic cell,

$$\delta W' = E\delta q \tag{9.13}$$

$$\left(Since\ W = VIt = Eq\ \Rightarrow\ \delta W = E\delta q\right)$$

[Where

E – Cell Emf

$\delta q -$ Infinitesimal quantity of electric charge transformed across the cell due to the chemical reaction in the cell.]

Again from the Faraday's law of electrolysis,

$$\delta q = ZFdn \tag{9.14}$$

$$\left(\begin{array}{c} Since\ Fraday's\ law, we\ know\ that \\ I \times t = \frac{F \times W}{A/Z} \Rightarrow q = ZF\left(\frac{W}{A}\right) = ZFn \\ \Rightarrow \delta q = ZFdn \end{array}\right)$$

[Where,

n – Number of moles]

Putting equation (9.14) in the equation (9.13), we will get

$$\delta W' = E \times (ZFdn) = ZFEdn \tag{9.15}$$

Again putting the equation (9.15) in equation (9.12), we will get

$$dG = -\delta W' = -ZFEdn \tag{9.16}$$

So for 1 mol of the above equation (9.16) becomes

$$dG = -ZFE \Rightarrow \Delta G = -ZFE \tag{9.17}$$

Similarly, at standard state equation (9.17) becomes

$$dG^0 = -ZFE^0 \Rightarrow \Delta G^0 = -ZFE^0 \tag{9.18}$$

Since we know

$$\Delta G = \Delta G^0 + RT \ln J \tag{9.19}$$

Now using equation (9.17) and (9.18) in the equation (9.19), we will get

$$-ZFE = -ZFE^0 + RT \ln J \tag{9.20}$$

$$\Rightarrow -E = -E^0 + \frac{RT}{ZF} \ln J \tag{9.21}$$

$$\Rightarrow E = E^0 - \frac{RT}{ZF} \ln J \tag{9.22}$$

The above equation (9.22) is known as **Nernst's equation**.

Equation (9.22) can be written as

$$E = E^0 - \frac{2.303RT}{ZF} \log J \tag{9.23}$$

9.3.1 Sign Convention for EMF:

Reaction 9.7: $Zn(S)/ZnSO_4\left(\underbrace{aq}_{Sat}\right)//CuSO_4\left(\underbrace{aq}_{Sat}\right)/Cu(S)$

a. Single vertical lines separate electrode from electrolyte. Double vertical lines represented the porous diaphragm.
b. If the reaction proceeds spontaneously from left to right, then the sign of the E will be positive and for reverse case right to left, sign of E is negative.

CHAPTER-10

MISCELLANEOUS

10.1 PHASE STABILITY DIAGRAMS:

Stoichiometric compounds are those in which elements are present in simple ratios.

Example: SiO_2, Al_2O_3 etc.

Non-stoichiometric compounds are those in which elements are not present in simple ratios. Moreover, the ratio depends on the temperature and pressure.

Example: Wustite (FeO)

- Reality, it is Fe_xO, where x varies from 0.86 to 0.97 depending upon the partial pressure of the O_2 in the surrounding.
- Again Fe exhibits two valences Fe^{2+} & Fe^{3+} ions depends on T and P_{O_2}.

10.1.1 Phase Stability Diagram for Ni-S-O System:

During process of roasting, generally elements like Ni, Cu, Pb, Zn etc. get converted from its sulphides to its oxides in the presence of oxidizing atmosphere.

In the roasting of Nickel Sulphide expected products are Ni, NiO, NiS, Ni_3S_3, $NiSO_4$.

Normally, there are four independent reactions occur such as

$$\text{Reaction 10.1: } Ni(s) + \frac{1}{2}O_2(g) = NiO(s)$$

$$Reaction\ 10.2\text{: } NiS(s) + \frac{3}{2}O_2(g) = NiO(s) + SO_2(g)$$

$$Reaction\ 10.3\text{: } NiO(s) + SO_2(g) + \frac{1}{2}O_2(g) = NiSO_4(s)$$

$$Reaction\ 10.4\text{: } 3NiS(s) + O_2(g) = Ni_3S_2(s) + SO_2(g)$$

Independent reaction means none of the above reaction depends upon the other three reactions. Since solids are pure, their activities are one. Hence, the equilibrium relations for the above reactions can be written as

$$Ni - NiO : \log P_{O_2} = -2\log K_1 \quad (10.1)$$

$$NiS - NiO : \log P_{SO_2} = \log K_2 + \frac{3}{2}\log P_{O_2} \quad (10.2)$$

$$NiO - NiSO_4 : \log P_{SO_2} = -\log K_3 - \frac{1}{2}\log P_{O_2} \quad (10.3)$$

$$NiS - Ni_3S_2 : \log P_{SO_2} = \log K_4 - \log P_{O_2} \quad (10.4)$$

Here P_{SO_2}, P_{O_2} are the values in equilibrium with the respective solids as shown above.

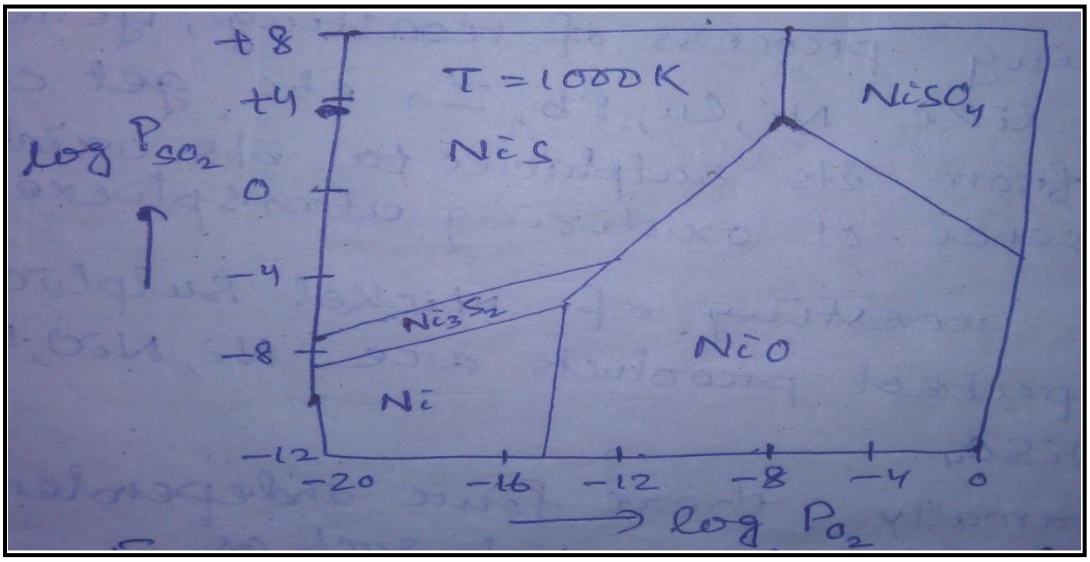

Fig 10.1: Phase stability diagram for Nickel-Sulpher-Oxygen System at 1000 K

The plotting based on equations (10.1-10.4). The straight lines correspond to two phase equilibria. The areas correspond to zones of stability of single solids. Such diagrams are also termed as Predominance area diagram by T. R. Ingraham (1967) who first constructed some of these including Ni-S-O system.

10.2 DEFECTS IN THERMODYNAMICS:

In ionic crystals, the formation of point defects or imperfections is subject to the requirement that the overall electrical neutrality is maintained.

i. An ion displaced from a regular site to an interstitial site is called a **Frankel imperfection**. Since cations are generally smaller ions, so there is possibility to displace into void space. Anions do not get displaced as cations as void space is just too small for their size. There is no change in overall electrical neutrality. Example: CaF_2, Silver halides etc.

ii. A pair of one cataion and one anion can be missing. The valence of missing pair of ions should be equal to maintain electrical neutrality. Such pair of vacant ion sites is called as **Schottky imperfection.**

10.3 THERMAL ANALYSIS:

10.3.1 Introduction:

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of temperature. The techniques include the measurement of temperatures at which changes may occur, the measurement of the energy absorbed (endothermic transition) or evolved (exothermic transition) during a phase transition or a chemical reaction, and the assessment of physical changes resulting from changes in temperature.

Various environments (vacuum, inert, or controlled gas composition) and heating rates from 0.1 to 500°C $\cdot$ min $^{-1}$ are available for temperatures ranging from −190 to 1400°C. The analysis of gases released by the specimen as a function of temperature is possible when thermal analysis equipment is coupled with Fourier-transform infrared detection or with a mass spectrometer.

The applications of thermal analysis are many and varied. For environmental measurements, these parameters can be measured: vapor pressure, thermal stability, flammability, softening temperatures, and boiling points. Compositional analysis offers phase diagrams, free versus bound water, solvent retention, additive analysis, mineral characterization, and polymer system analysis. In the important area of product reliability, thermal methods provide heat-capacity data, liquid-crystal transitions, solid fat index, purity, polymer cures, polymer quality control, glass transitions, Curie point, and fiber properties. Information on stability can be obtained from modulus changes, creep studies, expansion coefficients, and antioxidant evaluation. Dynamic properties of materials are found from viscoelastic measurements, impact resistance, cure characteristics, elastic modulus, loss modulus, and shear modulus. Lastly, chemical reactions can be followed through heats of transition, reaction kinetics, catalyst evaluation, metal–gas reactions, and crystallization phenomena.

10.3.2 Differential Scanning Calorimetry and Differential Thermal Analysis:

Differential scanning calorimetry (DSC) and quantitative differential thermal analysis (DTA) measure the rate and degree of heat change as a function of time or temperature. In addition to these direct energy measurements, the precise temperature of the sample material at any point during the experiment is also monitored.

Since DSC can measure both temperatures and heats of transitions or reactions, it has replaced DTA as the primary thermal analysis technique, except in certain high-temperature applications.

These methods are used to investigate the thermal properties of inorganic and organic materials. The procedure involves recording a temperature (DTA) or power (DSC) difference between a sample and a reference container as both are carried through a temperature program. DTA detects the physical and chemical changes that are accompanied by a gain or loss of heat in a substance as the temperature is altered. DSC provides quantitative information about any heat changes, including the rate of heat transfer.

When a thermal transition occurs in the sample, thermal energy is added either to the sample or the reference holders in order to maintain both the sample and reference at the sample temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy at the temperature of the transition.

Elevated pressure or reduced pressure is often beneficial to DSC experiments for such applications as the study of pressure-sensitive reactions, accelerated oxidation of lubricants or polymers, evaluation of catalysts, and resolution of overlapping transitions.

10.3.2.1 Instrumentation for DSC

In a cell designed for quantitative DSC measurements, two separate sealed pans, one containing the material of interest and the other containing an appropriate reference, are heated (or cooled) uniformly. The enthalpy difference between the two is monitored either at any one temperature (isothermal) or the temperature can be raised (or lowered) linearly. If maximum calorimetric accuracy is desired, the sample and reference thermocouples must be removed from direct contact with the materials.

The gradient temperature experiments can be run slowly ($0.1°C\cdot min^{-1}$) or rapidly (up to $300°C \cdot min^{-1}$). The electronic circuitry detects any change in heat flow in the sample versus the reference cell. This event in turn is sent as an analog signal to an output device such as a strip-chart recorder, digital integrator, or a computer. Information may be obtained with samples as small as 0.1 mg.

However, quantitative studies usually require at least 1 mg of sample. Expanding the upper temperature limit to 1500°C allows for DSC analyses to be done on materials such as ceramics, metal alloy systems, silicates, and high-temperature composites.

The DSC cell uses a constantan disk as the primary means of transferring heat to the sample and reference holders and also as one element of the temperature-sensing thermoelectric junction. Samples in powder, sheet, film, fiber, crystal, or liquid form are placed in disposable aluminum sample pans of high thermal conductivity and weighed on a microbalance. The sample is placed in one sample holder and an empty sample holder serves as reference. Sample sizes range from 0.1 to 100 mg.

The differential heat flow to the sample and reference through the disk is monitored by the chromel–constantan thermocouples formed by the junction of the constantan disk and the chromel wafer covering the underside of each platform. Chromel and alumel wires connected to the underside of the wafers form a chromel–alumel thermocouple, which is used to monitor the sample temperature. Thin-layer, large-area sample distribution minimizes thermal gradients and maximizes temperature accuracy and resolution.

Generally, holders are covered with domed, aluminum sample-holder covers. The covers are essentially radiation shields that enhance baseline linearity and reproducibility from run to run. An airtight sample-holder enclosure isolates the holders from external thermal disturbances and allows vacuum or controlled atmosphere operation. A see-through window permits observation of physical changes in unencapsulated samples during a scan. Side ports allow addition of catalysts and seeding of supercooled melts.

Three different DSC cells are available: standard (as described), dual sample, and pressure capability. The dual-sample cell provides an immediate twofold increase in sample throughput, while the pressure DSC cell provides capability from vacuum to 7 MPa (1000 $\text{lb}\cdot\text{in}^{-2}$).

10.3.2.2. <u>Instrumentation for DTA:</u>

In DTA a thermocouple is inserted into the center of the material in each sample holder. The sample is in one holder and reference material is placed in the other sample holder. The sample blocks are then heated. The difference in temperature between sample and reference thermocouples is continuously measured. Furnace temperature is measured by an independent thermocouple. Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature versus the programmed temperature indicates the transition temperature(s) and whether the transition is exothermic or endothermic. For high-temperature studies (1200 to 1600°C), the sample holders are fabricated from platinum Iridium.

10.3.2.3 Applications of DSC and DTA:

Applications include melting-point and glass transition measurements, curing studies, oxidative stability testing, and phase-transition studies.

1. *Glass Transition Temperature:*

The DSC trace of a polymeric material will show a step in the recorded signal by the polymer undergoing a second-order heat-capacity change at the glass transition temperature (T_g). As the temperature continues to increase, viscosity drops, and the polymer becomes mobile enough to realign into a crystalline structure. The heat released from the so-called "cold crystallization" produces an exothermic peak on the DSC curve. The area under the peak is proportional to the heat of crystallization. At higher temperatures the crystalline material melts, and an endothermic peak is recorded. The glass transition determines the useful lower temperature range of an elastomer, which is normally used well above this temperature to ensure the desired softness. In thermoset materials the glass transition temperature is related to the degree of cure, with the glass transition temperature steadily increasing as the degree of cure increases. Additionally, the glass transition temperature is often used to determine the storage temperature of uncured or partially cured material, since curing does not begin until the material is heated above its glass transition temperature.

2. *Crystallization and Fusion:*

The exothermal crystallization enthalpy as well as the endothermal heat of fusion (at −25°C) can be evaluated by integrating curve areas. In a semi crystalline polymer the crystallinity can be calculated from the measured heat of fusion, which is a characteristic property and widely used for quality control.

3. *Curing Reactions:*

During a curing reaction, energy is released from the sample as cross-linking occurs and a large exothermic peak follows the glass transition.

4. *Curie Point:*

An interesting application of DSC is the determination of the Curie point temperatures of ferromagnetic materials. Selected Curie point standards are alumel, 163°C; nickel, 354°C; and iron, 780°C.

5. *Oxidative Stability:*

DSC is a useful tool for generating data on oxidative stability of fats and oils. In either the isothermal or the temperature-programmed mode, the onset of a deviation from the baseline can be related to the oxidative induction period. In practice, the system would be brought to the test temperature and held isothermally in a nitrogen atmosphere. Oxygen is then introduced and the time necessary to give the first indication of oxidation (exotherm) is noted. DSC can differentiate quickly between stable and unstable systems and determine which antioxidant system would best preserve the specimen.

6. *Chemical Reactions:*

Depending upon the polymer and its intended use, various types of chemical reactions may be studied. Exotherms produced by polymerization, curing, oxidative degradation, and other reactions can be studied. Such information is useful in processing, in shelf-life estimates, and in hazards evaluation for energetic polymers.

In many cases it is possible to derive kinetics information from the DSC curves. One of the simplest and most broadly applicable methods is based upon the change in the DSC peak maximum temperature with heating rate. Samples are temperature-programmed at several rates (*β*) and the corresponding exothermic peak temperatures (*T*) are plotted as

$$\frac{d\log\beta}{d\left({}^{1}/_{T}\right)} = 1.912\left({}^{E}/_{R}\right) \tag{10.5}$$

Where E is the Arrhenius activation energy in joules per mole. The reaction frequency factor (*Z*) is calculated from the same curves as

$$Z = \frac{\beta E e^{\left({}^{E}/_{RT}\right)}}{RT^2} \tag{10.6}$$

The polymer reaction rate (k) at any temperature is available from the Arrhenius equation

$$k = Ze^{-\left({}^{E}/_{RT}\right)} \tag{10.7}$$

The equation for Z is a first-order form; however, the error incurred for other reaction orders is small and can usually be neglected.

10.3.3 THERMOGRAVIMETRIC ANALYSIS:

Thermo gravimetric analysis (TGA) monitors the change in mass of a substance as a function of temperature or time as the sample is subjected to a controlled temperature program. TGA has often been used to rank polymeric materials in order of their thermal stability by comparing losses of weight versus temperature. Many important TGA procedures involve isothermal monitoring of the mass loss from a material. Thus, when one or more isothermal holds are involved in the total heating program, the mass loss is often monitored versus time. In addition, plotting heating rate versus the temperature for a specified degree of conversion yields kinetic data for the decomposition process. The weight-loss method for determining kinetic values avoids difficulties that occur for DSC when exothermic and endothermic events coincide and interfere with the analysis.

A second use of TGA is the determination of the loss rate of moisture, diluents, and unreacted monomer that must be removed from the polymer. Polymers can also be pyrolyzed in the TGA equipment to enable determination of carbon black fillers or residual inorganic material. Another important use of TGA is in helping in the interpretation of DSC and DTA thermo grams. For example, early endothermic activity in a programmed DSC curve might represent low-melting-point polymer, or it may be due to volatilization of low-molecular-weight material. A TGA run would resolve the question.

10.3.3.1 TGA Instrumentation:

To perform TGA, the equipment must be capable of both simultaneous heating and weighing. Instrumentation includes the following:

i. A sensitive recording microbalance capable of detecting weight changes as small as 0.1 μg.

ii. A furnace and an appropriate enclosure for heating the sample specimen. For most applications the temperature range will be from ambient to 1000°C. A small low-mass designed furnace permits rapid linear heating and cooling rates as fast as 200°C per minute.

iii. A temperature programmer, heat-control circuitry, and associated electronics. Linear heating rates from 5 to 10°C·min $^{-1}$ are typical, although much higher rates are available. Many important TGA procedures involve isothermal monitoring of the mass loss from a material.

iv. A pneumatic system for dynamic purging of the furnace and sample chamber.

v. A data acquisition system.

Additional features might be a purge-gas switching capability for those applications in which the purge gas is changed during the experiment, and software to generate a first-derivative differential thermo gravimetric curve from the TG data after storage.

Thermal curves obtained by TGA offer what is probably the most accurate ordinate scale of weight or weight percent of all thermal analysis techniques. The temperature axis is often less well defined. First, the thermocouple is generally close but not in contact with the sample; also the dynamic gaseous atmosphere surrounding the TG sample may influence the sample temperature.

10.3.3.2 Applications of TGA:

Thermogravimetry provides the laboratory chemist with a number of important testing applications. The most important applications include compositional analysis and decomposition profiles of multi component systems studied at varying temperatures and atmospheric conditions, parameters that can be tailored and switched at any point during the experiment. Other important applications include the rapid proximate analysis of coal, quantitative separation of the main sample components in multi component mixtures, the determination of the volatile and moisture components in a sample material, kinetic studies, accelerated aging tests, and oxidation–reduction reactions.

Curie point measurements by TGA provide an accurate method for the calibration of the temperature axis of the thermogram since the Curie point temperature of many materials is well known and characterized. The ferromagnetic material is suspended in a magnetic field that is oriented such that a vertical component of magnetic force acts on the sample. This magnetic force acts as an equivalent magnetic mass on the TGA microbalance beam to indicate an apparent sample weight. When the sample is heated through its Curie point, the magnetic mass will be lost and the microbalance will indicate an apparent weight loss.

Moisture determination is an important application of TGA. In many industries even small amounts of moisture have serious consequences. When the sample is rapidly heated to 105°C and held at this temperature, any moisture present in the sample is lost. Moisture levels at 0.5% and often below can be determined.

Determination of the temperature of oxidation of a sample is another TGA application. For example, if magnesium powder is heated from 300 to 900°C in an oxidizing (air) atmosphere, at approximately 682°C a sharp increase in sample weight is noted that corresponds to the rapid oxidation of the material.

10.4 HOMOGENEOUS & HETEROGENEOUS EQUILIBRIA:-

In reversible chemical reactions, the forward and reverse reactions are competing with each other and have different reaction rates. The rates are dependent on time and on the concentrations of the reagents and products. Chemical equilibrium is when the chemical rate of reaction is equal in both directions.

10.4.1 Types of Equilibrium:

The concept of equilibrium applies to any chemical reaction in any phase of matter. Solution equilibria can be divided into two subsets: homogeneous-solution equilibria and heterogeneous-solution equilibria.

10.4.1.1 Homogeneous equilibria:

In the equilibrium reactions, if all the reactants and the products are in same phase, then it is said to be in homogeneous equilibria.

Reaction 10.5: C_2H_5OH (l) + CH3COOH (l) $\rightleftharpoons$ $CH_3COOC_2H_5$ (l) + H_2O (l)

Reaction 10.6: N_2 (g) + 3 H_2 (g) $\rightleftharpoons$ 2 NH_3 (g)

Reaction 10.7: 2 SO_2 (g) + O_2 (g) $\rightleftharpoons$ $2SO_3$ (g)

10.4.1.2 Heterogeneous equilibria:

In the equilibrium reactions, if both the reactants and the products are in different phases, then it is said to be in heterogeneous equilibria.

Reaction 10.8: $2NaHCO_3$ (s) $\rightleftharpoons$ Na_2CO_3(s) + CO_2 (g) + H_2O (g)

Reaction 10.9: Ca $(OH)_2$ (s) + H_2O(l) $\rightleftharpoons$ Ca^{2+}(aq) + $2OH^{-}$(aq)

Reaction 10.10: $CaCO_2$(s) $\rightleftharpoons$ CaO (s) + CO_2 (g)

10.5 CONTROLLED ATMOSPHERE (CA):

A controlled atmosphere is an agricultural storage method. An atmosphere in which Oxygen, Carbon dioxide and Nitrogen concentrations as well as temperature and humidity regulated.

CA storage is a non-chemical process. Oxygen levels in the sealed rooms are reduced, usually by the infusion of nitrogen gas, from the approximate 21 percent in the air we breathe to 1 percent or 2 percent. Temperatures are kept at a constant 32 to 36 degrees Fahrenheit. Humidity is maintained at 95 percent and carbon dioxide levels are also controlled. Exact conditions in the rooms are set according to the product variety. Researchers develop specific regimens for each variety to achieve the best quality. CA storage has come a long way since then, and researchers in Washington State have been among the leaders in this technology. CA was first used in the United States in the 1960s and Washington now has the largest capacity of CA storage of any growing region in the world. The large, airtight CA rooms vary in size from 10,000 boxes to 100,000 boxes, depending on the volume of fruits produced and upon its marketing strategies. Apples take in oxygen and give off carbon dioxide as starches in the flesh change to sugar. In the sealed rooms, this respiratory process reduced the oxygen, thus slowing the ripening process. Computers help keep conditions constant.

Two major classes of commodity can be stored in controlled atmosphere:

i. Dry commodities such as grains, legumes and oilseed. In these commodities the primary aim of the atmosphere is usually to control insect pests. Most insects cannot exist indefinitely without oxygen or in conditions of raised (greater than approximately 30%) carbon dioxide. Controlled atmosphere treatments of grains can be a fairly slow process taking up to several weeks at lower temperatures (less than 15°C). A typical schedule for complete disinfestations of dry grain (<13% moisture content) at about 25°C, with carbon dioxide, is a concentration above 35% carbon dioxide (in air) for at least 15 days. These atmospheres can be created either by:
    - Adding pure gases carbon dioxide or nitrogen or the low oxygen exhaust of hydrocarbon combustion, or
    - Using the natural effects of respiration (grain, moulds or insects) to reduce oxygen and increase carbon dioxide Hermetic storage.

ii. Fresh fruits, most commonly apples and pears, where the combination of altered atmospheric conditions and reduced temperature allow prolonged storage with only a slow loss of quality.

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