Chemical Thermodynamics S.Y.BSc.

Concept of Gibb's free energy and Helmholtz free energy

a) **Gibb's free energy**:

1) It was introduced by J.Willard Gibb's to account for the work of expansion due to volume change in chemical process , while explaining the concept of maximum work.

2) It is represented by the symbol 'G'.

3) It is defined as, $\mathbf{G = H - TS}$

4) It is a state function because enthalpy(H), entropy(S) and temperature (T) are state functions.

5) It is also defined as energy available to do useful work.

6) It is a property that provides a convenient measure of driving force of the reaction.

7) When a system changes from one state to another, the net available energy under specified conditions results from decrease in Gibb's free energy of the system.

8) The Gibb's free energy change ΔG is related to enthalpy change ΔH and entropy change ΔS by the relation $\mathbf{\Delta G = \Delta H - T\Delta S}$.

9) For a spontaneous chemical reaction to occur, ΔG must be negative.

10) For a chemical reaction at equilibrium, the equilibrium constant is related to free energy change by the relation $-\Delta G = RT\ln K_p$

This equation suggest that for a spontaneous change, K_p value becomes very large indicating that the reaction proceeds to a maximum extent in forward direction.

b) Helmholtz free energy:

1) It is represented by the symbol A and is defined as , $\mathbf{A = U - TS}$

Where, U is the internal energy of the system
T is temperature of the system
S is Entropy of the system.

2) As entropy, temperature and internal energy are state functions, Helmholtz free energy is also a state function.

3) For any chemical reaction, the total internal energy is not utilized to do useful work. Some part of this energy is lost to bring about the entropy change. If ‘dS’ is the entropy change, then the energy lost is given by,

$$\mathbf{dS = \frac{dq_{rev}}{T} \therefore\ dq_{rev} = T \cdot ds} \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

If the energy in the above equation(1) is subtracted from the total energy **dE** of the system, then the remaining energy will be useful to do work at constant temperature from the system. It is this energy which is called Helmholtz free energy or work function.

4) For a process carried out at constant temperature, the maximum work done by the system is obtained at the expense of decrease in Helmholtz free energy or work function.

<u>Relation between Gibb’s free energy and Helmholtz free energy</u>:

Gibb’s free energy is defined as **G** = **H – TS**

For a system undergoing change at constant temperature, the free energy change ΔG is given by, $\mathbf{\Delta G = \Delta H - T\Delta S}$ **………………(**1)

Helmholtz free energy (A) is defined as , **A = U – TS**

For a system undergoing change at constant temperature, the change in the Helmholtz free energy is given by ,

$$\mathbf{\Delta A = \Delta U - T\Delta S} \ldots\ldots\ldots\ldots\ldots(2)$$

But enthalpy change for a chemical reaction at constant pressure is given by,

$$\mathbf{\Delta H = \Delta U + P\Delta V} \ldots\ldots\ldots\ldots\ldots(3)$$

Substituting (3) in equation (1) we get,

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

ie. $\Delta G = \Delta U - T\Delta S + P\Delta V$

Since , $\Delta A = \Delta U - T\Delta S$ from equation (2), we get

$$\mathbf{\Delta G = \Delta A + P\Delta V}$$

The Gibb's free energy change differ from Helmholtz free energy change by work of expansion ie. $P\Delta V$

Significance of Gibb's free energy

A chemical reaction is governed by three important thermodynamic state functions:

a) Enthalpy change Δ **b)** Entropy change ΔS **c)** Gibb's free energy change ΔG

The above three are related by the equation $\mathbf{\Delta G = \Delta H - T\Delta S}$-----------(I)
Equation (I) has a great significance as it decides the spontaneity of a process. For a reaction to be spontaneous, the free energy change must be negative. However, the sign of free energy depends upon the sign of ΔH and ΔS. hence four distinct cases arises:

	Sign of ΔH	**Sign of ΔS**	**Sign of ΔG**	**Remark**
I	– ve Exothermic	+ ve Endothermic	Always –ve	Reaction is spontaneous at all temperatures
II	+ ve Endothermic	– ve Decrease in entropy	Always +ve	Reaction is non-spontaneous at all temperatures
III	– ve Exothermic	– ve Decrease in entropy	Depends upon temperature: i) At low temperature $T\Delta S < \Delta H$ ii) At high temperature at $T > T_i$ where, $T_i = \frac{\Delta H}{\Delta S}$	Reaction is spontaneous at low temperature. Reaction is non-spontaneous at high temperature.
IV	+ ve Endothermic	+ ve increase in entropy	Depends upon temperature: i) At low temperature $T\Delta S < \Delta H$ ii) At high temperature	Reaction is non-spontaneous at low temperatures Reaction is

			$T\Delta S > \Delta H$	spontaneous at high temperature

In general , one can conclude that the sign of ΔG helps to decide the nature of process as shown below:

$\Delta G < 0$ process is spontaneous
$\Delta G > 0$ process is non-spontaneous
$\Delta G = 0$ process has reached equilibrium

Variation of Gibb's free energy with temperature and pressure or Show that $\left(\frac{\delta G}{\delta T}=\right)_T = V$ and $\left(\frac{\delta G}{\delta T}=\right)_P = T$

Gibb's free energy is defined as $G = H - TS$ --------------(i)
where, H is the enthalpy of the system
T is absolute temperature
S is Entropy of the system

For infinitesimal change, equation (i) can be written as,

$dG = dH - SdT - TdS$ -------------- (ii)

By definition $H = U + PV$; $dH = dU + VdP + PdV$ ------------(iii)

fFom the first law of thermodynamics,

$dU = dq + dW$

If work is of expansion type, then $dw = - PdV$ therefore,

$$dU = dq_{rev} - PdV$$

If the process is reversible , then for a closed system

$dq_{rev} = - PdV$ -------------------(iv) and $dq_{rev} = T.dS$

where, dS is infinitesimal entropy change for a reversible process

substituting (iii) and (iv) in the equation (i) we get,

$$dG = dU + PdV + VdP - dq_{rev} - SdT$$
$$= dq_{rev} - PdV + PdV + VdP - dq_{rev} - SdT$$
$$= VdP - S.dT \text{-----------------(vi)}$$

At constant pressure, $dP = 0$

$$dG = - S.dT$$

$$\left(\frac{\delta G}{\delta T}\right)_P = -S$$

The rate of change of Gibb's free energy with temperature at constant pressure is equal to decrease in entropy of the system.

At constant temperature, dT = 0

$$dG = VdP$$

$$\left(\frac{\delta G}{\delta T}\right)_T = V$$

Thus the rate of change of Gibb's free energy with respect to pressure at constant temperature is equal to increase in volume occupied by the system.

Gibb's-Helmholtz's equation and its application

Gibb's free energy is defined as

G = H – TS ----------------(1)

Where, H is the enthalpy of the system
T is absolute temperature
S is Entropy of the system

Enthalpy H is defined by the equation:

H = U + PV -------------(2) U internal energy of the system
P pressure
V volume occupied by the system

Substituting (2) in equation (1) we get,

G = U + PV – TS -----------(3)

Differentiating equation (3) on both sides we get,

dG = dU + PdV + VdP – TdS – SdT ------------(4)

From 1st law for a reversible process

$dU = dq_{rev} + dW$

If the work is of expansion type then,

dW = – P.dV

therefore, $dU = dq_{rev} – P.dV$ ----------------------(5)

By definition, $dS = \frac{dq_{rev}}{T}$ $\therefore dq_{rev} = T.dS$ ----------------(6)

Substituting (5) and (6) in equation (4) we get,

$dG = dq_{rev} – P.dV + PdV – dq_{rev} – S.dT + VdP$

dG = V.dP – S.dT -----------------(7)

At constant pressure, $dP = 0$

Therefore , $dG = -S.dT$ --------------(8)

Consider a system in which the following reaction occurs at constant pressure:

$$\mathbf{A_{(reactant)}} \rightarrow \mathbf{B_{(product)}}$$

Let S_1 and S_2 be the entropies of the reactant and product respectively. If G_1 and G_2 are the free energies of A and B respectively then from equation 8, we get

$$dG_1 = -S_1dT \quad \text{and} \quad dG_2 = -S_2dT$$

therefore, $dG_2 - dG_1 = -S_2dT - (-S_1dT)$

$$d(G_2 - G_1) = -S_2dT + S_1dT$$

$$\text{ie. } d(\Delta G) = -(S_2 - S_1)dT$$

$$d(\Delta G) = -\Delta S dT$$

therefore, $\Delta \mathbf{S} = -\frac{\mathbf{d(\Delta G)}}{\mathbf{dT}}$ -----------------(9)

But, $\Delta G = \Delta H - T\Delta S$ ------------------(10)

Substituting (9) in equation 10 ,we get

$$\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_P \text{-----------------(11)}$$

Equation (11) is called Gibbs – Helmholtz equation. The term $\left[\frac{d(\Delta G)}{dT}\right]_P$ is called temperature coefficient of free energy change.

Applications :

1) It is applicable for calculation of ΔG for all process occurring at constant pressure.

2) It helps to calculate emf of the reversible cell.

3) One can use this equation of a reversible cell for a reaction if free energy changes at two different temperatures are known.

Concept of phase equilibrium and Clapeyron equation

The various process which involve phase transitions are vaporization, evaporation, condensation, fusion etc. In all these processes, there is no new substance formed. When substances involved in these processes are in pure state, then after some time, these processes reach equilibrium at constant temperature and pressure. Thus we say that phases are in equilibrium with each other. This is possible if $\Delta G = 0$, where ΔG is the free energy change accompanying the process.

Consider the following equilibrium between two phases A and B.

$$\boldsymbol{A_{phase} \rightleftharpoons B_{phase}}$$

If G_A and G_B are the free energies of A and B per mole respectively, then

$$\Delta G_{T,P} = G_B - G_A$$

But at equilibrium , $\Delta G_{T,P} = 0$

Therefore, $G_B = G_A$

Thus when two phases of the same single substance are in equilibrium at a given temperature and pressure, then their molar free energy is same in each phase.

Clapeyron Equation:

Consider the following equilibrium between two phases A and B of the same substance at a given temperature.

$$\boldsymbol{A_{phase} \rightleftarrows B_{phase}}$$

Let G_A and G_B are the free energies per mole of A and B per mole respectively, then

At equilibrium , $G_A = G_B$ -----------------(1)

Now if the temperature is changed from T to T + δT, then the free energies of A and B will also change to $G_A + dG_A$ and $G_B + dG_B$ respectively. The system will again reach equilibrium, so

$$G_A + \delta G_A = G_B + \delta G_B$$

But $G_A = G_B$ (from equation -1)

Hence, $dG_A = dG_B$ -------------(2)

But $dG = V.dP - S.dT$ --------------------(3)

Therefore, $dG_A = V_A.dP - S_A.dT$ ------(4) and $dG_B = V_B.dP - S_B.dT$ ----(5)

Substituting equation (4) and (5) in equation (2) we get,

$$V_A.dP - S_A.dT = V_B.dP - S_B.dT$$

$$(V_B - V_A)dP = (S_B - S_A)dT$$

Therefore, $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$

But $\Delta \mathbf{S} = \frac{\Delta H}{T}$ where ΔH is molar latent heat of phase change occurring at temperature T

Therefore, $\frac{dP}{dT} = \frac{\Delta H}{T(\Delta V)}$ -----------------(6)

Equation (6) is known as Clapeyran equation.

Clausius – Clapeyron equation and its applications

Consider the following type of equilibrium between two phases of same substance at constant temperature and pressure.

liquid ⇄ vapour

If G_A and G_B are the free energies of liquid and vapour state respectively, then

$$\mathbf{G_A = G_B} \text{ -----------------(1)}$$

If the temperature of the system is changed from T to T + dT with the corresponding change in pressure from P to P + dP, then

G_A becomes $G_A + dG_A$ and G_B becomes $G_B + dG_B$

After the change, again the two phases remain in equilibrium,

ie. $G_A + dG_A = G_B + dG_B$

But since $G_A = G_B$

Hence, $dG_A = dG_B$ -------------(2)

But $dG = V.dP - S.dT$ --------------------(3)

Hence, $dG_A = V_A.dP - S_A.dT$ ------(4) and

$dG_B = V_B.dP - S_B.dT$ ------(5)

From equation (2), we have,

$$V_A.dP - S_A.dT = V_B.dP - S_B.dT$$

Therefore, $(V_B - V_A)dP = (S_B - S_A)dT$

$$\Delta V.dP = \Delta S.dT$$

Therefore, $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ -----------(6)

But, $\Delta S = \frac{\Delta H}{T}$

Hence $\frac{dP}{dT} = \frac{\Delta H}{T(\Delta V)}$ -----------------(7)

Equation (7) is known as Clapeyron equation.

In terms of liquid- vapour equilibrium, equation (7) can be written as

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_v - V_l)} \text{------------(8)}$$

Where, ΔH_v is molar heat of vaporization of the substance

V_v volume of vapour

V_l volume of liquid

Clausius modified Clapeyron equation suggesting the following things.

i) For vapourization and sublimation, $V_v >>>> V_l$, therefore volume of liquid can be neglected

ii) Assume the vapours to behave ideally.

Applying the above modification to equation (8) , we ge

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_v} \text{------------(9)}$$

For one mole of a vapour behaving ideally,

$$PV_v = RT$$

$$V_v = \frac{RT}{P} \quad \text{----------(10)}$$

Substituting equation (10) in equation (9) we get

$$\frac{dP}{dT} = \frac{\Delta H_v.P}{RT^2} \text{------------(11)}$$

On rearranging equation (11) we get

$$\frac{dP}{P} = \frac{\Delta H_v.dT}{RT^2} \text{------------(12)}$$

Or

$$\frac{dlnP}{dT} = \frac{\Delta H_v}{RT^2} \text{------------(13)}$$

Equation (13) is known as Clausius – Clapeyron equation.

If P_1 and P_2 are the vapour pressure at temperature T_1 and T_2 respectively, then integrating equation (13) (assuming ΔH_v to remain constant over the temperature range, we get,

$$\int_{P_1}^{P_2} dlnP = \frac{\Delta H_v}{R}\int_{T_1}^{T_2} \frac{1}{T^2}\,d\,T$$

$$\text{ie.}\quad ln\frac{P_2}{P_1} = -\frac{\Delta H_v}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\text{ie.}\quad ln\frac{P_2}{P_1} = +\frac{\Delta H_v}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\mathbf{log}\frac{\boldsymbol{P_2}}{\boldsymbol{P_1}} = \frac{\boldsymbol{\Delta H_v}}{\boldsymbol{2.303R}}\left(\frac{\mathbf{1}}{\boldsymbol{T_2}}-\frac{\mathbf{1}}{\boldsymbol{T_1}}\right) - - - - - - - (\mathbf{14})$$

Equation (14) is the integrated form of Claussius – Clopeyron equation.

Applications:

i) It help to calculate ΔH_v if P_1 , P_2 and T_1 and T_2 are known.

ii) One can also calculate T_2 if P_1 , P_2, T_1 and ΔH_v are known.

Verification of Claussius Clapeyron equation

For a liquid – vapour equilibrium , Claussius – Clapeyron equation is,

$$\frac{\boldsymbol{dlnP}}{\boldsymbol{dT}} = \frac{\boldsymbol{\Delta H_v}}{\boldsymbol{RT^2}}\text{------------}(1)$$

Where ΔH_v is the molar heat of vapourization.

On rearranging equation(1) and integrating it we get,

$$\int dlnP = \frac{\Delta H_v}{R}\int \frac{1}{T^2}\,dT$$

$$lnP = -\frac{\Delta H_v}{R} + c - - - - - - (2)$$

Where '*c*' is the constant of integration.

Converting equation (2) to $\log_{10}$ we get,

$$\log P = -\frac{\Delta H_v}{2.303RT} + c' \quad \text{or}$$

$$\log P = \frac{-B}{T} + c' \quad \text{------------------------}(3)$$

where B = $\frac{\Delta H_v}{2.303RT}$

When a graph of lop P v/s 1/T is plotted, a straight line is obtained with slope = – B. this verifies Claussius – Clapeyron equation.

Partial molal property of a system

A system is characterized by the following two properties.

a) **Extensive property** : It is a property which depends upon the amount of matter present in the system eg. mass, volume

b) **Intensive property** : It is a property which is independent of the amount of matter present in the system. Eg. pressure, temperature.

Any change in the extensive property is brought about by change in temperature or pressure. For a closed or isolated system, the mass and composition of the system remains unchanged. However , for an open system, mass and composition of the system may vary. Therefore to define total extensive property of a system, the change in mass and composition of the constituents also contribute to a significant extent. Hence, G.N. Lewis introduced the concept of partial molal property for the study of open system.

Partial molal property of a component in a system is defined as the change in magnitude of extensive property due to addition of the mole of that component to such a large quantity of the system that the added mole does not bring about any significant change in temperature, pressure and composition of the system.

Consider an extensive property X of a system consisting of two component 1 and 2 . Let n_1 and n_2 be the number of moles of the components of the system. The property X is a function of temperature, pressure , n_1 and n_2. ie

$$X = f(T , P , n_1 , n_2)$$

If a small change is made in temperature , pressure and no. of moles of the components, then the change in extensive property dX is given by, dX = $\left(\frac{dX}{dT}\right)_{Pn_1n_2} dT + \left(\frac{dX}{dP}\right)_{Tn_1n_2} dP + \left(\frac{dX}{dn_1}\right)_{TPn_2} dn_1 + \left(\frac{dX}{dn_2}\right)_{TPn_1} dn_2$ ----------(1)

At constant temperature and pressure dT = 0 and dP = 0

Therefore **dX =** $\boldsymbol{\left(\frac{dX}{dn_1}\right)_{TPn_2} dn_1 + \left(\frac{dX}{dn_2}\right)_{TPn_1} dn_2}$-------------------------------(2)

The term $\frac{dX}{dn_1}$, $\frac{dX}{dn_2}$ in equation (2) are referred to as partial molal quantities with reference to components 1 and 2 respectively.

Representation of partial molal property

$$\overline{X_1} = \left(\frac{dX}{dn_1}\right)_{TPn_2}$$

$$\overline{X_2} = \left(\frac{dX}{dn_2}\right)_{TPn_1}$$

For a system containing two components

dX = $\overline{X_1}$ dn_1 + $\overline{X_2}$ dn_2

for a system of 'i' constituents at const temperature and pressure,

dX = $\overline{X_1}$ dn_1 + $\overline{X_2}$ dn_2 + -------------+ $\bar{X}_i dn_i$

Partial molal volume

Consider a binary solution obtained by mixing n_1 moles of compound 1 and n_2 moles of compound 2. Since volume is an extensive property, its magnitude depends upon temperature, pressure and no. of moles of the components present in solution.

ie. **V = *f*(T , P , n_1 , n_2)**

If a change is made in temperature , pressure and no. of moles of the components of the solution , then the change in extreme property dV is given by,

dV = $\left(\frac{dV}{dT}\right)_{Pn_1n_2} dT + \left(\frac{dV}{dP}\right)_{Tn_1n_2} dP + \left(\frac{dV}{dn_1}\right)_{TPn_2} dn_1 + \left(\frac{dV}{dn_2}\right)_{TPn_1} dn_2$

At constant temperature and pressure dT = 0 and dP = 0

Therefore dV = $\left(\frac{dV}{dn_1}\right)_{TPn_2} dn_1 + \left(\frac{dV}{dn_2}\right)_{TPn_1} dn_2$

The term $\left(\frac{dV}{dn_1}\right)_{TPn_2}$ and $\left(\frac{dV}{dn_2}\right)_{TPn_1}$ are referred to as partial molal volume of components 1 and 2 respectively. It is represented as $\bar{V}_1$ and $\bar{V}_2$ respectively.

Therefore, dV = $\bar{V}_1$ dn_1 + $\bar{V}_2$ dn_2

For a system of ith components,
dV = $\bar{V}_1$ dn_1 + $\bar{V}_2$ dn_2 + -------------+ $\bar{V}_i dn_i$

Thus partial molal volume is defined as change in volume of the system at constant temperature and pressure when one mole of a compound is added to such a large volume of a solution that the added mole does not bring any change in the concentration of the solution.

Concept of Chemical potential.

The term chemical potential for a pure substance refers to a driving force which determines whether a substance will undergo a chemical reaction or not. It is also called partial molal free energy. For a pure substance, chemical potential is equal to free energy per mole.

Free energy is an extensive property. For a system consisting of 'i' constituents, if n_1, n_2 , n_3 ,……n_i are the number of moles of the constituents 1 ,2 ,3 ,…..,i respectively, then the free energy G is given by G = *f*(T , P , n_1 , n_2 , …….n_i)

A small change in temperature , pressure and no. of moles brings a change in free energy, which is given by,

dG = $\left(\frac{dG}{dT}\right)_{Pn_1n_2\ldots n_i} dT + \left(\frac{dG}{dP}\right)_{Tn_1n_2\ldots n_i} dP + \left(\frac{dG}{dn_1}\right)_{TPn_2\ldots n_i} dn_1 + \ldots \left(\frac{dG}{dn_i}\right)_{TPn_1,n_2\ldots n_i} dn_i$

At constant temperature and pressure dT = 0 and dP = 0

Therefore

dG = $\left(\frac{dG}{dn_1}\right)_{TPn_2,n_3\ldots n_i} dn_1 + \left(\frac{dG}{dn_2}\right)_{TPn_1,n_2\ldots n_i} dn_2 + \left(\frac{dG}{dn_i}\right)_{TPn_1,n_2\ldots n_i} dn_i \ldots.(1)$

The term, $\left(\frac{dG}{dn_i}\right) dn_i$ refers to partial chemical potential for ith component and is represented as $\overline{G_i}$ and $\overline{\mu_i}$.

Therefore , dG = $\overline{G_1}$ dn$_1$ + $\overline{G_2}$ dn$_2$ + -------------+ $\bar{G}_i$dn$_i$ or

$$dG = \overline{\mu_1}\, dn_1 + \overline{\mu_2}\, dn_2 + \text{-------------} + \bar{\mu}_i dn_i \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Thus chemical potential of the component may be defined as the change in Gibbs free energy of a system that results when one mole of the component '*i*' is added to a large quantity of the system at constant temperature and pressure without bringing any change in the composition of the system.

If the system has definite composition, then equation (2) on integration gives,

$$\mathbf{G = \mu_1 n_1 + \mu_2 n_2 + \ldots\ldots\ldots + \mu_i n_i} \text{ ------------}(4)$$

For a system of only one component, equation (4) becomes,

$$G = \mu_1 n_1$$

If n_1 = 1 mole, then μ_1 = G

Thus for one mole of the constituent, chemical potential is same as Gibb's free energy.

Gibbs-Duhem equation.

Consider a system consisting of 'i' constituents. Let $\mathbf{n_1, n_2, n_3, \ldots\ldots n_i}$ are the number of moles of the component **1 ,2 ,3 ,.....,i** respectively. If G is the free energy of the system then G, being an extensive property, will be a function of temperature ,and no. of moles of the various constituents of the system.

ie G = *f*(T , P , n$_1$, n$_2$, ...n$_i$)

By changing temperature , pressure and no. of moles of the constituents, the change in free energy, which is given by,

$$\mathbf{dG} = \left(\frac{dG}{dT}\right)_{Pn_1n_2\ldots n_i} dT + \left(\frac{dG}{dP}\right)_{Tn_1n_2\ldots n_i} dP + \left(\frac{dG}{dn_1}\right)_{TPn_2\ldots n_i} dn_1 + \left(\frac{dG}{dn_2}\right)_{TPn_1,n_2\ldots n_i} dn_2 + \cdots \ldots . \left(\frac{dG}{dn_i}\right)_{TPn_1,n_2\ldots n_i} dn_i \text{---------------------}\mathbf{(1)}$$

At constant temperature and pressure dT = 0 and dP = 0

$$\therefore dG = \left(\frac{dG}{dn_1}\right)_{TPn_2,n_3\ldots n_i} dn_1 + \left(\frac{dG}{dn_2}\right)_{TPn_1,n_2\ldots n_i} dn_2 + \cdots \ldots \left(\frac{dG}{dn_i}\right)_{TPn_1,n_2\ldots n_i} dn_i \text{---}(2)$$

But $\left(\frac{dG}{dn_1}\right) = \overline{G_1} = \mu_1$ = chemical potential of component 1

$\left(\frac{dG}{dn_2}\right) = \overline{G_2} = \mu_2$ = chemical potential of component 2

Hence equation (2) can be written as,

$dG = \mu_1 dn_1 + \mu_2 dn_2 + \dots\dots\dots + \mu_i dn_i$ ------------(3)

Integrating equation (3) we get,

$(G)_{T,P} = \mu_1 n_1 + \mu_2 n_2 + \dots\dots\dots + \mu_i n_i$ ------------(4)

Differentiating equation (4) we get,

$(dG)_{T,P} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \dots\dots\dots + \mu_i dn_i + n_i d\mu_i$
$= (\mu_1 dn_1 + \mu_2 dn_2 + \dots\dots\dots + \mu_i dn_i) + (n_1 d\mu_1 + n_2 d\mu_2 + \dots\dots\dots + n_i d\mu_i)$-------(5)

Substituting equation (3) in equation (5) we get,

$dG = dG + (n_1 d\mu_1 + n_2 d\mu_2 + \dots\dots\dots + n_i d\mu_i)$

ie $n_1 d\mu_1 + n_2 d\mu_2 + \dots\dots\dots + n_i d\mu_i = 0$............................(6)

or $\sum n_i d\mu_i = 0$.........................(7)

Equation (7) is known as Gibbs-Duhem equation.

For a two component system, equation (6) can be written as

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

Therefore $d\mu_1 = -\frac{n_2}{n_1} d\mu_2$ ------------------(8)

Equation (8) is another form of Gibbs-Duhen equation for a binary mixture. This equation indicates that a change in chemical potential of one component causes a corresponding change in chemical potential of another component.

Variation of chemical potential of a substance change with change in temperature and pressure

Ans. The chemical potential of the ith constituent of a system is given by,

$\mu_i = \left(\frac{dG}{dn_i}\right)_{TPn_1,n_2\ldots n_i} = \overline{G}_{\mathrm{i}} \ldots\ldots.(1)$

Variation of chemical potential with temperature:

Differentiating equation (1) with respect to temperature at constant pressure we get,

$$\left(\frac{d\mu_i}{dT}\right)_{P,n_i} = \frac{d}{dt}\left(\frac{dG}{dn_i}\right)_{P,n_i} = \left(\frac{d^2}{dTdn_i}\right)_{P,n_i} \quad \dots\dots(2)$$

We know that dG = Vdp – SdT

At constant pressure , dP = 0

Therefore. dG = – S.dT or $\left(\frac{\boldsymbol{dG}}{\boldsymbol{dT}}\right)_{\boldsymbol{P}} = \boldsymbol{-S}$ $\quad \dots\dots\dots\dots\dots(3)$

Differentiating equation (3) w.r.t. n_i at constant T,P and n_i we get,

$$\frac{\boldsymbol{d}}{\boldsymbol{dn}_{\mathbf{i}}}\left(\frac{\boldsymbol{dG}}{\boldsymbol{dT}}\right)_{\boldsymbol{P,n_i}} = -\left(\frac{\boldsymbol{dS}}{\boldsymbol{dn_i}}\right)_{\boldsymbol{T,P,n_i}}$$

ie. $\left(\frac{\boldsymbol{d^2G}}{\boldsymbol{dn_idT}}\right)_{\boldsymbol{P,n_i}} = -\left(\frac{\boldsymbol{dS}}{\boldsymbol{dn_i}}\right)_{\boldsymbol{T,P,n_i}} = \boldsymbol{-\overline{S}_{\mathbf{i}}} \dots\dots(\mathbf{4})$,

where $\overline{S}_{\mathrm{i}}$ = partial molal entropy

Comparing equation (2) and equation (4) we get,

$$\left(\frac{\boldsymbol{d\mu_i}}{\boldsymbol{dT}}\right)_{\boldsymbol{P,n_i}} = \boldsymbol{-\overline{S}_{\mathbf{i}}} \dots\dots\dots(5)$$

Thus the rate of chemical potential of the ith constituent with temperature at constant pressure is equal to decrease in partial molal entropy of ith constituent.

Variation of chemical potential with respect to pressure:

Differentiating equation (1) with respect to pressure at constant temperature we get,

$$\left(\frac{d\mu_i}{dP}\right)_{T,n_i} = \frac{d}{dt}\left(\frac{dG}{dn_i}\right)_{T,n_i} = \left(\frac{d^2}{dP.dn_i}\right)_{T,n_i} \quad \dots\dots(6)$$

We know that dG = Vdp – SdT

At constant temperature , dT = 0

Therefore, dG = VdP

ie. $\left(\frac{dG}{dP}\right)_T = V \dots\dots\dots\dots\dots(7)$

Differentiating equation (7) w.r.t. n_i at constant T,P and n_i we get,

$$\boldsymbol{\frac{d}{dn_{\mathrm{i}}}\left(\frac{dG}{dP}\right)_{T,P,n_i} = -\left(\frac{dV}{dn_i}\right)_{T,P,n_i}}$$

ie. $\left(\boldsymbol{\frac{d^2G}{dn_i dP}}\right)_{\boldsymbol{T,P,n_i}} = -\left(\boldsymbol{\frac{dV}{dn_i}}\right)_{\boldsymbol{T,P,n_i}} = \boldsymbol{\bar{V}_{\mathrm{i}}} \ldots\ldots (\mathbf{8})$,

where $\bar{V}_{\mathrm{i}}$ = partial molal volume of ith component.

Comparing equation (6) and equation (8) we get,

$$\left(\boldsymbol{\frac{d\mu_i}{dP}}\right)_{\boldsymbol{T,n_i}} = \boldsymbol{\bar{V}_{\mathrm{i}}} \ldots\ldots\ldots (5)$$

ie. **the rate of change of chemical potential of the ith constituent with pressure at constant temperature is equal to the partial molal volume of the ith constituent**.