

**Thermodynamics:**

[Paper V: Physical Chemistry, 09 lectures]

It is the study of energy transformations involved in the processes.

1<sup>st</sup> law: The total energy of the universe remains constant.

2<sup>nd</sup> law: the entropy of the universe is always increasing.

Statements to remember:

$H=E+PV$	$PV=RT$
$q_{rev}=dE+W_{rev}$	$q_{rev}/T =dS$

**Spontaneity:** Spontaneous processes are natural processes and hence occur with increase in entropy. Hence entropy was selected as measure of the spontaneity. But it was found inconvenient, so two new functions are introduced as Gibb’s free energy [G] and Helmholtz free energy [A].

Mathematically these can be derived as follows:

Total heat content or enthalpy = Available energy + unavailable energy $H=$ free energy + TS $H=G+TS$ $G=H-TS$ -----[1] The change in the G at constant T is given by $\Delta G = \Delta H - T\Delta S$ -----[2]	Internal energy = Available energy + unavailable energy $E=$ free energy + TS $E=A+TS$ $A=E-TS$ -----[1'] The change in the A at constant T is given by $\Delta A = \Delta E - T\Delta S$ -----[2']
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**Significance of the Helmholtz free energy:**

$A=E-TS$ -----[2]

Differentiating this equation we get:  $dA=dE-TdS-SdT$ -----[3]

But we know,  $q_{rev}=dE+W_{rev}$  and  $q_{rev}/T =dS$  hence,  $q_{rev}=TdS$  and  $dE= TdS- W_{rev}$  -----

Putting this value in eqn. [3] we get:

$dA= TdS- W_{rev} -TdS-SdT$

$dA= - W_{rev} -SdT$ -----[4]

so at constant temperature,  $dT=0$  hence, eqn [4] becomes:

$[dA]_T = -W_{rev}$  OR  $-[dA]_T = +W_{rev}$  -----[5] this gives significance of Helmholtz free energy ie. the decrease in Helmholtz free energy at constant temperature is the maximum reversible work done by the system.

**Significance of the Gibb's free energy:**

$$G=H-TS-----[2]$$

Also we know,  $H=E+PV$

Hence  $G=E+PV-TS-----[3]$

Differentiating this equation we get:  $dG=dE+PdV+VdP-TdS-SdT-----[3]$

But we know,  $q_{rev}=dE+W_{rev}$  and  $q_{rev}/T =dS$  hence,  $q_{rev}=TdS$  and  $dE= TdS- W_{rev}$  where  $W_{rev}$  is the sum of mechanical and nonmechanical work done by the system.

$$W_{rev}= W_{mechanical} +W_{nonmechanical}$$

OR  $W_{rev}= PdV+W_{net}$

so,  $dE= TdS- PdV-W_{net}$

putting this value in the eqn [3] we get:  $dG= TdS- PdV-W_{net} +PdV+VdP-TdS-SdT$

$$dG= -W_{net} +VdP -SdT -----[4]$$

1. at constant P and T,  $dP$  and  $dT=0$

hence  $dG= -W_{net}$  OR  $-[dG]_{T,P}=W_{net}$  -----[5] This gives significance of Gibb's free energy ie. the decrease in Gibb's free energy at constant temperature and pressure is the maximum nonmechanical or Net work done by the system.

2. In isolated system where  $W_{net}=0$ , we have eqn [4] as:

$$dG= VdP -SdT -----[6]$$

2a.] At constant pressure,  $dP=0$  and so,  $[dG]_P= SdT$

$[dG/dT]_P=-S$  for the change in free energies at different temperatures,  $[dG/dT]_P = -\Delta S$

Putting this value of  $-S$  in equation  $\Delta G = \Delta H - T\Delta S-----[1']$  we have

$$\Delta G = \Delta H - T[d\Delta G/dT]_P -----[7] \text{ is called Gibb's Helmholtz equation.}$$

2b] At constant temperature,  $dT=0$  and so,  $[dG]_T = VdP$

For 1 mole of ideal gas  $PV=RT$  . so,  $dG= RT/P dP$ -----[8]

Integrating this equation within the limits of  $G_1$  and  $G_2$ ,  $P_1$  and  $P_2$  we get,

$$G_2-G_1= RT [\ln P_2-\ln P_1]$$

$\Delta G= RT \ln[P_2/P_1] \text{ OR } \Delta G= 2.303 RT \log[P_2/P_1] \text{ -----[9]}$
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**Clapyeron's equation:** It is the application of thermodynamics to the Phase equilibria. It gives the effect of pressure on the transition temperature. Eg. Liquid is in equilibrium with the vapours at the B.P. so as the change in free energy for the process in equilibrium is zero. Hence if free energy of Liquid is  $G_L$  and that of vapours is  $G_V$  then

$$G_L=G_V$$
-----[1]

If pressure is changed from  $P$  to  $P+dP$  then  $T$  also changes from  $T$  to  $T+dT$  and also the free energies. Now when the new equilibrium is established, we have,

$$G_L+dG_L=G_V+dG_V$$

From eqn. 1,  $dG_L= dG_V$ -----[2]

We have  $dG= Vdp-SdT$  hence  $V_Ldp-S_LdT= V_Vdp-S_VdT$

$$S_VdT-S_LdT= V_Vdp-V_Ldp$$

$$(S_V-S_L) dT= (V_V-V_L)dp$$

$$dP/dT= (S_V-S_L)/ (V_V-V_L) \text{ but } \Delta S=Q_{vap}/T$$

hence we have

$\frac{dP}{dT} = \frac{Q_{vap}}{T(V_V-V_L)}$
--

this is Clapyeron's equation.

Clusius further simplified this equation by assuming two things:

1. The volume of liquid is negligible as compared to that of vapours.  $V_L \ll V_V$  and  $V_V - V_L = V_V = V$
2. the vapours behave as ideal gas. Hence  $PV=RT$ .

Now the Clapeyron eqn becomes:

$$\frac{dP}{dT} = \frac{Q_{vap}}{TV} = \frac{Q_{vap}}{T \frac{RT}{P}} = \frac{PQ_{vap}}{RT^2}$$

$$\frac{dP}{P} = \frac{Q_{vap}}{RT^2} dT$$

Integrating this eqn. within the limits P<sub>1</sub>,P<sub>2</sub> and T<sub>1</sub>,T<sub>2</sub>, we have

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{Q_{vap}}{RT^2} dT$$

$$\ln P_2 - \ln P_1 = \frac{-Q_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln P_2/P_1 = \frac{-Q_{vap}}{R} \left[ \frac{T_1 - T_2}{T_1 T_2} \right]$$

$$2.303 nR \log P_2/P_1 = Q_{vap} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log_{10} \frac{p_2}{p_1} = \frac{Q_{vap}}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

this is *Clausius Clapeyron equation*.

Thermodynamic derivation of law of mass action:

The law of mass action states that ‘the rate of reaction is proportional to the product of active masses of the reactants.’

i.e For a reaction : A+B=C+D

Rate of forward reaction  $\propto [A][B]$  and Rate of backward reaction  $\propto [C][D]$

Hence, at the equilibrium when

Rate of forward reaction =Rate of backward reaction,

Equilibrium constant is given by:

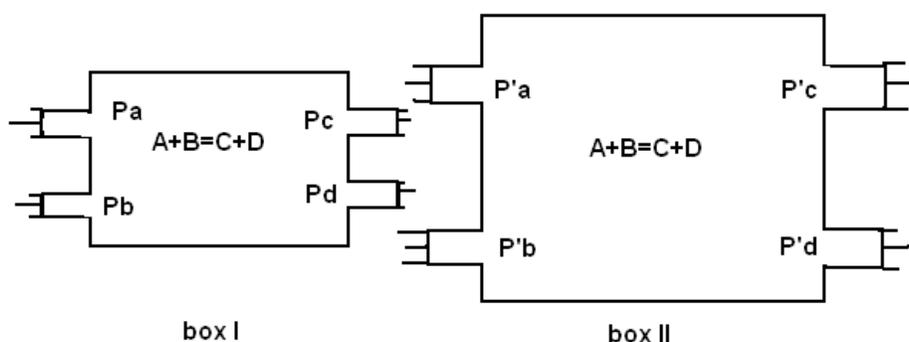
$$K = \frac{[C][D]}{[A][B]}, \quad K = \frac{P_C P_D}{P_A P_B}, \quad K = \frac{C_C C_D}{C_A C_B}$$

Where, [ ] = active mass,

In case of gases their pressure and in case of solutions their concentration is considered as active mass.

For the derivation of law of mass action, it is assumed that

1. All the reactants and products are ideal gases [so that laws of Thermodynamics can be applied]
2. The reaction occurs in hypothetical equilibrium boxes as given in the figure.
3. The volume of the boxes is so large that little addition or removal of the gases will not change the composition. [There is no work done due to addition/removal of gases]
4. The partial pressures of A,B,C and D in box I are  $P_a$ ,  $P_b$ ,  $P_c$  and  $P_d$ , & those in box II are  $P'a$ ,  $P'b$ ,  $P'c$  and  $P'd$  respectively.



Suppose the following steps are carried out.

1. One mole of A is removed from box I and introduced in box II after changing its pressure from  $P_a$  to  $P'_a$
2. One mole of B is removed from box I and introduced in box II after changing its pressure from  $P_b$  to  $P'_b$
3. One mole of C is removed from box II and introduced in box I after changing its pressure from  $P'_c$  to  $P_c$
4. One mole of D is removed from box II and introduced in box I after changing its pressure from  $P'_d$  to  $P_d$

The changes in free energy during these four steps are given by:

$$\Delta G = RT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$$

ie.

$$\Delta G_A = RT \ln \frac{P'_a}{P_a} \quad \text{--- [1]} \quad \Delta G_C = RT \ln \frac{P_c}{P'_c} \quad \text{--- [3]}$$

$$\Delta G_B = RT \ln \frac{P'_b}{P_b} \quad \text{--- [2]} \quad \Delta G_D = RT \ln \frac{P_d}{P'_d} \quad \text{--- [4]}$$

The total change in free energy is given by:  $\Delta G = \Delta G_A + \Delta G_B + \Delta G_C + \Delta G_D$

$$\Delta G = RT \ln \frac{P'_a}{P_a} + RT \ln \frac{P'_b}{P_b} + RT \ln \frac{P_c}{P'_c} + RT \ln \frac{P_d}{P'_d}$$

$$\Delta G = RT \ln \frac{P'_a P'_b}{P_a P_b} + RT \ln \frac{P_c P_d}{P'_c P'_d}$$

As, for the reaction in equilibrium, the net change in free energy is zero,

$$RT \ln \frac{P'_a P'_b}{P_a P_b} + RT \ln \frac{P_c P_d}{P'_c P'_d} = 0$$

$$RT \ln \frac{P'_a P'_b}{P_a P_b} = - RT \ln \frac{P_c P_d}{P'_c P'_d}$$

$$\frac{P'_a P'_b}{P_a P_b} = \frac{P'_c P'_d}{P_c P_d} \quad \text{i.e.} \quad \boxed{\frac{P_c P_d}{P_a P_b} = \frac{P'_c P'_d}{P'_a P'_b} = \text{constant} = K}$$

-----Law of Mass Action.

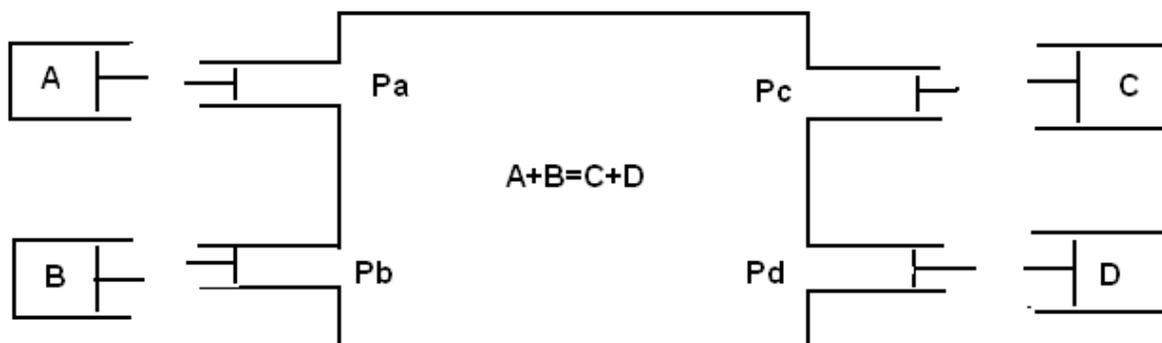
**Van't Hoff isotherm:**

[Application of thermodynamics to reaction to calculate the free energy change/work done during a reaction]

Consider a reaction  $A+B=C+D$

Where assume that:

1. All the reactants and products are ideal gases [so that laws of Thermodynamics can be applied]
2. The reaction occurs in hypothetical equilibrium box as given in the figure.
3. The volume of the box is so large that little addition or removal of the gases will not change the composition.
4. The partial pressures of A,B,C and D in box I are  $P_a$ ,  $P_b$ ,  $P_c$  and  $P_d$ , & those in pure form are  $P^0_a$ ,  $P^0_b$ ,  $P^0_c$  and  $P^0_d$  respectively.



**van't Hoff equilibrium box**

Suppose the following steps are carried out.

1. One mole of A at  $P^0_a$ , introduced in box after changing its pressure from  $P^0_a$  to  $P_a$
2. One mole of B at  $P^0_b$  is introduced in box after changing its pressure from  $P^0_b$  to  $P_b$

3. One mole of C at  $P_c$  is removed from box and compressed to  $P^0_c$ .

4. One mole of D at  $P_d$  is removed from box and compressed to  $P^0_d$

As, change in free energy when one mole of gas is expanded/compressed

$$\Delta G = RT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$$

Is given by

The changes in free energy during these four steps are given by:

$$\Delta G_A = RT \ln \frac{P_a}{P'a} \quad \text{--- [1]} \quad \Delta G_C = RT \ln \frac{P'c}{P_c} \quad \text{--- [3]}$$

$$\Delta G_B = RT \ln \frac{P_b}{P'b} \quad \text{--- [2]} \quad \Delta G_D = RT \ln \frac{P'd}{P_d} \quad \text{--- [4]}$$

The total change in free energy is given by:  $\Delta G = \Delta G_A + \Delta G_B + \Delta G_C + \Delta G_D$

$$\Delta G = RT \ln \frac{P_a}{P'a} + RT \ln \frac{P_b}{P'b} + RT \ln \frac{P'c}{P_c} + RT \ln \frac{P'd}{P_d}$$

$$\Delta G = RT \ln \frac{P_a P_b P'c P'd}{P'a P'b P_c P_d}$$

$$\Delta G = RT \ln \frac{P_a P_b}{P_c P_d} + RT \ln \frac{P'c P'd}{P'a P'b}$$

$$\Delta G = -RT \ln \frac{P_c P_d}{P_a P_b} + RT \ln \frac{P'c P'd}{P'a P'b}$$

When  $P_c, P_d, P_a, P_b$  are equilibrium pressures,

$$K_p = \frac{P_c P_d}{P_a P_b}$$

and if  $P^0_a, P^0_b, P^0_c$  and  $P^0_d=1$  then  $\Delta G = \Delta G^0$

Hence,  $\Delta G^0 = -RT \ln K_p$  OR  $-\Delta G^0 = RT \ln K_p$

But  $-\Delta G = W_{net} = W_{max} - P\Delta V$

Therefore,  $W_{max} = RT \ln K_p + P\Delta V$

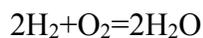
For n moles of ideal gas  $P\Delta V = \Delta nRT$

where  $\Delta n =$  number of moles of products - number of moles of reactants

hence,

$W_{max} = RT \ln K_p + \Delta nRT = 2.303 RT \log K_p + \Delta nRT$ -----[van't Hoff isotherm]
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We can apply this eqn to reactions as:



Number of reactant molecules = 3, number of product molecules = 2

$\Delta n =$  number of moles of products - number of moles of reactants = 2 - 3 = -1

Hence  $W_{max} = RT \ln K_p + \Delta nRT = 2.303 RT \log K_p - RT$

3. For the reaction  $N_2 + 3H_2 = 2NH_3$   $\Delta n = 2 - 4 = -2$

4. For the reaction  $CO + H_2O = CO_2 + H_2$   $\Delta n = 2 - 2 = 0$

Problem:

1. Standard free energy change of the reaction



at 298 K is  $-22770 \text{ joules.mol}^{-3}$ . Calculate the equilibrium constant for this reaction at 298K. ( $R = 8,314 \text{ JK}^{-1}\text{mol}^{-1}$ )

solution: given  $\Delta G^0 = -22770 \text{ joules.mol}^{-3}$  hence  $\Delta G^0 = -22770 / 3 \text{ joules per mole}$

$$\Delta G^0 = -7590 \text{ joules per mole}$$

2. Calculate the free energy change accompanying the reaction  $H_2+I_2=2HI$  at  $443^{\circ}C$ , if the value of the equilibrium constant at  $443^{\circ}C$  is 50.62.

Given  $K_p=50.62$ ,  $T=443+273=716K$ ,  $R=8.314J$ ,  $-\Delta G=?$

$-\Delta G=2.303 RT\log K_p$ , **Answer:  $\Delta G = -23366.2$  Joules**

**Van't Hoff isochore:**

This is equation obtained by combining van't hof isotherm and Gibb's Helmholtz equation.

We have  $\Delta G^0 = -RT \ln K_p$  -----[1]

Differentiating this equation w.r.t. T at constant pressure we have,

$$\left[ \frac{d\Delta G^0}{dT} \right]_p = -R \ln K_p - RT \left[ \frac{d \ln K_p}{dT} \right]_p$$
 -----[2]

Multiplying this eqn by T we have

$$T \left[ \frac{d\Delta G^0}{dT} \right]_p = -RT \ln K_p - RT^2 \left[ \frac{d \ln K_p}{dT} \right]_p$$
 -----[3]

But  $\Delta G^0 = -RT \ln K_p$

Hence

$$T \left[ \frac{d\Delta G^0}{dT} \right]_p = \Delta G^0 - RT^2 \left[ \frac{d \ln K_p}{dT} \right]_p$$
 -----[4]

Gibb's Helmholtz eqn at standard state is

$$\Delta G^0 = \Delta H^0 + T \left[ \frac{d\Delta G^0}{dT} \right]_p$$

i.e

$$T \left[ \frac{d\Delta G^0}{dT} \right]_p = \Delta G^0 - \Delta H^0 \text{-----[5]}$$

where  $\Delta H^0$  is enthalpy change of reaction carried out in standard state.  $\Delta H^0 \approx \Delta H$

Comparing equations 4 and 5 we have

$$\Delta H = RT^2 \left[ \frac{d\ln K_p}{dT} \right]_p$$

$$\frac{d\ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

$$d\ln K_p = \frac{\Delta H}{RT^2} dT$$

If  $\Delta H$  is constant over a range of temperatures then, integrating eqn within the limits  $K_{p1}$  and  $K_{p2}$ ,  $T_1$  and  $T_2$ , we have.

$$\int_{K_{p1}}^{K_{p2}} d\ln K_p = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT$$

$$\ln \frac{K_{p2}}{K_{p1}} = - \frac{\Delta H}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\log_{10} \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

-----[6]this is van't Hoff isochore  
which can be used to determine any one of the  $K_{p1}, K_{p2}, T_1, T_2$  and  $\Delta H$ .

Problem: The equilibrium constant  $K_p$  for a reaction at 643K is  $3.3 \times 10^{-4}$  and at 703K is  $8.6 \times 10^{-5}$ . Calculate the enthalpy change for the reaction

( $R=8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ).

Given :  $K_{p1} = 3.3 \times 10^{-4}$   $K_{p2} = 8.6 \times 10^{-5}$   $T_1 = 643\text{K}$   $T_2 = 703\text{K}$   $\Delta H = ?$

**Answer:**  $\Delta H = -842426 \text{ Joules}$

**Fugacity and activity:** The equations like van's Hoff isotherm and isochore are applied to gaseous reactions at low pressure and relatively high temperatures, as the gases are nearly ideal. But for other conditions, i.e. at high pressure and low temperature,  $PV \neq RT$ .

The equation for law of mass action can be applied to find free energy change of reactions in solution at lower concentrations. But for solutions too, the eqn is not fully valid at higher concentrations.

This deviation from ideal behavior is explained by Lewis : it is due to fugacity which is the escaping tendency of every substance from the existing state to other state. It is defined mathematically as

$dG = nRT \ln f$  where  $f$  is fugacity.

$dG = nRT \ln f$ Integrating this eqn we have $G = nRT \ln f + C$ When $f=1$ , $C=G^0$ $G = G^0 + nRT \ln f$	$dG = nRT \ln f$ Integrating this eqn within limits $G_1, G_2$ and $f_1, f_2$ we have $G_2 - G_1$ where $f_1, f_2$ are fugacities in initial and final state.
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When we compare fugacities of substances in a given state with standard state then above eqn becomes:  $\Delta G = nRT \ln f / f^\theta$ , this ratio of fugacities in the given state to standard state is called activity

$$\text{Activity} = a = f / f^\theta$$

Activity can also be defined as concentration of active part of the substance. i.e. if C is concentration and  $\gamma$  is activity coefficient or dissociation constant then

$$A = C \times \gamma$$

**Problem:** Vapour pressure of pure liquid is 100 torr at 298K while its vapour pressure from a 95mole percent solution at the same temperature is 90torr. What is the activity and activity coefficient of the liquid in the solution?

**Given:** standard fugacity  $f^\theta = 100$  torr, fugacity of 95mole percent solution = 90torr,

$$\text{Hence activity } a = f / f^\theta = 90 / 100 = 0.90$$

Concentration of the solution C=95, a=0.90 hence  $A = C \times \gamma$ ,

$$\gamma = A / C = 0.90 / 0.95 = 0.9473$$

**Partial molar quantities:** The magnitude of an extensive property such as E,G,S etc is dependent on the amounts of the constituents of the system, as well as T and P. Hence for open system, where the transfer of matter is allowed, the extensive property X is a function of T,P and number of moles of all constituents.

$$X = f(T, P, n_1, n_2, n_3, \dots) \dots \dots \dots [1]$$

For a small change in the system, the change in the extensive property is a complete differential of above eqn.

$$dX = \left( \frac{dX}{dT} \right)_{P, n_1, n_2, n_3, \dots} dT + \left( \frac{dX}{dP} \right)_{T, n_1, n_2, n_3, \dots} dP + \left( \frac{dX}{dn_1} \right)_{P, T, n_2, n_3, \dots} dn_1 + \left( \frac{dX}{dn_2} \right)_{P, T, n_1, n_3, \dots} dn_2 + \left( \frac{dX}{dn_3} \right)_{P, T, n_1, n_2, \dots} dn_3 \dots [2]$$

Thus the change in the extensive property due to addition or removal of a constituent I is called partial molar quantity

$$\bar{X}_1 = \left( \frac{dX}{dn_1} \right)_{P, T, n_2, n_3, \dots} \quad \bar{X}_2 = \left( \frac{dX}{dn_2} \right)_{P, T, n_1, n_3, \dots}$$

In general for  $i^{\text{th}}$  constituent,

$$\bar{X}_i = \left( \frac{dX}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots}$$

where,  $n_j$  means the number of moles of all constituents except I is held constant.

If X represents E,H,V,G,S etc. then we have:

$$\bar{E}_i = \left( \frac{dE}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots} \quad \bar{H}_i = \left( \frac{dH}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots} \quad \bar{V}_i = \left( \frac{dV}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots}$$

$$\bar{G}_i = \left( \frac{dG}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots} \quad \bar{S}_i = \left( \frac{dS}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots}$$

Thus we can have partial molar internal energy, partial molar enthalpy, partial molar volume, partial molar free energy, partial molar entropy etc.

**Partial molar volume:** partial molar volume is defined as the change in V when 1 mole of component i is added to an large amount of solution or mixture at constant T and P, keeping all other constituents unchanged.

$$\bar{V}_i = \left( \frac{dV}{dn_i} \right)_{P,T,n_1,n_3 \dots n_j \dots}$$

**Gibbs-Duhem equation:** The extensive property is given by eqn [2] as

$$dX = \left( \frac{dX}{dT} \right)_{P,n_1,n_2,n_3 \dots} dT + \left( \frac{dX}{dP} \right)_{T,n_1,n_2,n_3 \dots} dP + \left( \frac{dX}{dn_1} \right)_{P,T,n_2,n_3 \dots} dn_1 + \left( \frac{dX}{dn_2} \right)_{P,T,n_1,n_3 \dots} dn_2 + \left( \frac{dX}{dn_3} \right)_{P,T,n_1,n_2 \dots} dn_3$$

Where ,

$$\bar{X}_1 = \left( \frac{dX}{dn_1} \right)_{P,T,n_2,n_3,\dots} \quad \bar{X}_2 = \left( \frac{dX}{dn_2} \right)_{P,T,n_1,n_3,\dots}$$

Putting this in eqn [2] we have,

$$dX = \left( \frac{dX}{dT} \right)_{P,n_1,n_2,n_3,\dots} dT + \left( \frac{dX}{dP} \right)_{T,n_1,n_2,n_3,\dots} dP + \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + \bar{X}_3 dn_3$$

At constant temperature and pressure, we have

$$dX = \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + \bar{X}_3 dn_3 \quad \dots\dots\dots[3]$$

on integrating this eqn we have

$$X = \bar{X}_1 n_1 + \bar{X}_2 n_2 + \bar{X}_3 n_3 \quad \dots\dots\dots[4]$$

thus X is the contribution per mole of each particular constituent to the total value of the property X in the system under consideration.

Differentiating eqn [4] we have

$$dX = \bar{X}_1 dn_1 + n_1 d\bar{X}_1 + \bar{X}_2 dn_2 + n_2 d\bar{X}_2 + \dots\dots\dots$$

$$dX = \left( \bar{X}_1 dn_1 + \bar{X}_2 dn_2 \dots\dots \right) + \left( n_1 d\bar{X}_1 + n_2 d\bar{X}_2 + \dots \right) \quad \dots\dots\dots[5]$$

Comparing equations [3] and [5] we have

$$\left( n_1 d\bar{X}_1 + n_2 d\bar{X}_2 + \dots \right) = 0$$

$$\sum n_i d\bar{X}_i = 0$$

i.e.  $\sum n_i d\bar{X}_i = 0$  is called Gibbs Duhem equation.

For binary mixture,

$$n_1 d\bar{X}_1 = - n_2 d\bar{X}_2$$