

Solution Thermodynamics

There is a accompanying change in energy if a solution is formed.

$$\text{Total mass } M = \sum_i^n x_i M_i$$

(Gibbs Free energy)

$$d(nG) = nVdP - nsdT \quad \dots \dots (1)$$

This indicates the total gibbs free energy change of any closed system

$$\text{Now, } \left(\frac{\partial nG}{\partial P} \right)_{T, n_i} = nV \quad \text{and} \quad \left(\frac{\partial nG}{\partial T} \right)_{P, n_i} = ns$$

For a feasible process, $\Delta S > 0$
 $\Delta G < 0$

For a single phase open system materials may go into and out of the system and nG becomes a function of the no of moles of the chemical species (n_i)

$$\text{Hence } nG = f(T, P, n_1, n_2, \dots, n_i) \quad \dots \dots (3)$$

$$d(nG) = \left(\frac{\partial nG}{\partial P} \right)_{T, n_i} dP + \left(\frac{\partial nG}{\partial T} \right)_{P, n_i} dT + \sum_i \left(\frac{\partial nG}{\partial n_i} \right)_{T, P, n_j} dn_i$$

Now the term,

$$\left(\frac{\partial nG}{\partial n_i} \right)_{P, T, n_j} = \mu_i \quad (\text{chemical potential.})$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \sum_i \mu_i dn_i$$

when we consider one mole of species, $n=1$.

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \sum_i \mu_i dn_i; \quad \dots \quad (1)$$

Comparing (i) and (4)

$$V = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} \cancel{dP} \quad - S = \left(\frac{\partial G}{\partial T}\right)_{P, n_i}$$

$$H = G + TS$$

$$H = G - T \left(\frac{\partial G}{\partial T}\right)_{P, n_i}$$

$[x_i = \text{mole fraction}]$

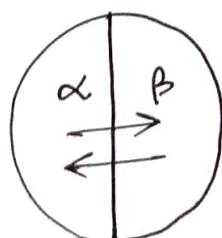
Chemical Potential and Equilibrium

For a closed single phase system containing chemically reactive species, all differentials dn_i must result from chemical reaction.

$$\sum_i \mu_i dn_i = 0 \quad (\text{If accumulation is not happening})$$

Multiphase system:

With respect to phase equilibrium we knew for a closed non reacting system consisting of ~~two~~ two phases in equilibrium each phase is open to other.



The materials can travel through phases for that Gibbs free energy will change.

For α -phase,

$$(dn_G)^\alpha = (nv)^\alpha dp - (ns)^\alpha dT + \sum \mu_i^\alpha dn_i \quad \dots (i)$$

For β -phase

$$(dn_G)^\beta = (nv)^\beta dp - (ns)^\beta dT + \sum \mu_i^\beta dn_i \quad \dots (ii)$$

Therefore on each, total system properties is expressed by,
 $n_M = (n_M)^\alpha + (n_M)^\beta$

Here M maybe any thermodynamic property.

$$d(n_G) = d(n_G)^\alpha + d(n_G)^\beta$$

at equilibrium constant temperature and pressure.

$$\sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta = 0$$

$$dn_i^\alpha = -dn_i^\beta$$

Since the movement is due to mass transfer only. It means same amt of materials is transferred.

$$\sum (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

Now dn_i^α cannot be zero because if it is zero that means no mass is transferring.

Hence $(\mu_i^\alpha - \mu_i^\beta) = 0$

$$\boxed{\mu_i^\alpha = \mu_i^\beta}$$

This is the fundamental condition for equilibrium.

Partial Properties :-

Partial properties of the i th species in solution

$$\partial \bar{M}_i = \left(\frac{\partial nM}{\partial n_i} \right)_{T, P, n_j} \rightarrow \text{Response function.}$$

Solution property is denoted by M

Partial property is denoted by \bar{M}_i

Pure species property is denoted by M_i

$$\text{Therefore } \bar{G}_i = \left(\frac{\partial nG}{\partial n_i} \right)_{T, P, n_j} = M_i$$

Chemical potential of i th species

= Partial \Rightarrow Gibbs free energy

For one mole of i th species total molar property is given by

$$dM = \left(\frac{\partial M}{\partial P} \right)_{T, x_i} dP + \left(\frac{\partial M}{\partial T} \right)_{P, x_i} dT + \sum \left(\frac{\partial M}{\partial x_i} \right)_{P, T, \cancel{x_j}} dx_i \\ = \left(\frac{\partial M}{\partial P} \right)_{T, x_i} dP + \left(\frac{\partial M}{\partial T} \right)_{P, x_i} dT + \sum \bar{M}_i dx_i \quad \dots (i)$$

$$M = \sum x_i \bar{M}_i \quad] \text{Summability equation.}$$

$$nM = \sum n_i \bar{M}_i$$

$$dM = \sum x_i d\bar{M}_i + \sum \bar{M}_i dx_i \quad \dots (ii)$$

from equation (i) and (ii)

$$\sum x_i d\bar{M}_i = \left(\frac{\partial M}{\partial P} \right)_{T, x_i} dP + \left(\frac{\partial M}{\partial T} \right)_{P, x_i} dT$$

This is Gibbs Duhem equation.

If the temp and press remains constant

$$\sum x_i d\bar{M}_i = 0$$

Partial Properties in a binary solution

$$M = x_1 \bar{M}_1 + x_2 \bar{M}_2$$

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2 \quad \text{--- (i)}$$

where M is a function of x at constant T and P

The appropriate form of Gibbs-Duhem equation at equilibrium

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \quad \text{--- (ii)}$$

As there is only two component the addition of their mole fraction is 1.

$$x_1 + x_2 = 1$$

$$x_2 = (1 - x_1)$$

Thus,

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + (\cancel{x_2} d\bar{M}_2) + \cancel{- \bar{M}_2 dx_1}$$
$$= (x_1 d\bar{M}_1 + x_2 d\bar{M}_2) + (\bar{M}_1 - \bar{M}_2) dx_1$$

→ This zero according to G.D equation.

$$\frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2$$

$$\bar{M}_2 = \frac{M - x_1 \bar{M}_1}{x_2} ; \quad \frac{dM}{dx_1} = \bar{M}_1 - \frac{M - x_1 \bar{M}_1}{x_2}$$

 $M = x_1 \bar{M}_1 + x_2 \bar{M}_2$

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$M_1 = M - x_2 M_2$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

From equation (ii) the Gibbs-Duhem equation can be written as, $x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0$

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0$$

$$\frac{dM_1}{dx_1} = - \frac{x_2}{x_1} \frac{dM_2}{dx_1}$$

Fugacity and fugacity coeff.

From the definition of μ_i , if y_i or $P \rightarrow 0$
 $\mu_i \rightarrow -\infty$

$$\begin{aligned} dG_i^{ig} &= \nu_i^g dP \\ &= \frac{RT}{P} dP = RT d(\ln P) \text{ at const } T. \end{aligned}$$

on integration, $G_i^{ig} = RT \ln P + f_i(T) \quad \text{--- (i)}$

$$\mu_i = \bar{G}_i^{ig} = RT \ln(y_i P) + f_i(T) \quad \text{--- (ii)}$$

Therefore fugacity for real fluid is given by

$$G_i = RT \ln(f_i) + f_i(T) \quad \text{--- (iii)}$$

→ Fugacity of i th component.

For ideal gases

Fugacity = Total pressure.

The fugacity of pure species 'i' can be expressed in various forms,

Subtracting (iii) from (i)

$$G_i - G_i^{ig} = RT \ln \left(\frac{f_i}{P} \right)$$

This indicates the deviation from ideal behavior.

$$\phi_i = \frac{f_i}{P} = \text{Fugacity coeff.}$$

$$G_i - G_i^{ig} = RT \ln \phi_i$$

$$\text{For all gases } \ln \phi_i = \int_0^P (z_i - 1) \frac{dp}{P} \quad \text{at constant } T$$

z_i = compressibility factor.

$$(z_i - 1) = \frac{B_{ii} P}{RT} \quad [B_{ii} = \text{second virial equation of state}]$$

$$\ln (\phi_i) = \int_0^P \frac{B_{ii} P}{RT} \frac{dp}{P}$$

$$= \frac{B_{ii} P}{RT}$$

Vapour-liquid Equilibrium for pure species :-

$$G_i = RT \ln (f_i) + \Gamma_i (T)$$

This equation defines the fugacity of pure species.

$$G_i^v = RT \ln (f_i^v) + \Gamma_i (T)$$

$$G_i^L = RT \ln (f_i^L) + \Gamma_i (T)$$

Subtracting these equation,

$$G_i^v - G_i^L = RT \ln \left(\frac{f_i^v}{f_i^L} \right)$$



This represents the energy required to convert saturated vapour to saturated liquid at constant temp and pressure.

therefor at constant temp and pressure

$$G_i^v - G_i^L = 0$$

$$RT \ln \left(\frac{f_i^v}{f_i^L} \right) = 0 ;$$

$$f_i^v = f_i^L = f_i^{\text{sat}}$$

This expresses the fundamental principle for a pure species consisting liq and vap phases are in equilibrium

where $f_i^v = f_i^L$

$$\phi_i^v = \phi_i^L = \phi_i^{\text{sat}}$$

Fugacity and Fugacity coeff for species in solution :-

For species 'i' in a mixture of real gas or in a solution of liq. The ideal gas state expression,

$$\mu_i = RT \ln \hat{f}_i + f_i(T)$$

\hat{f}_i is the fugacity of i th species in solution.

Therefore for multiphase system all phases in equilibrium or at same temperature and

$$\hat{f}_i^\infty = \hat{f}_i^\alpha = \hat{f}_i^\beta = \dots$$

Thus multiple phases at the same temp and pressure are in equilibrium when the fugacity in each constituent species is same in all phases.

Residual Property :-

$$\pi M^R = \pi M_i - \pi M_i^{ig}$$

By differentiating with respect to n_i at constant T and P we get,

$$\left[\frac{\partial \pi M^R}{\partial n_i} \right]_{T, P, n_j} = \left[\frac{\partial \pi M_i}{\partial n_i} \right]_{T, P, n_j} - \left[\frac{\partial \pi M_i^{ig}}{\partial n_i} \right]_{T, P, n_j}$$

$$\overline{M}_i^R = \overline{M}_i - \overline{M}_i^{ig}$$

Replacing M by G

$$\overline{G}_i^R = \overline{G}_i - \overline{G}_i^{ig}$$

$$\mu_i - \mu_i^{ig} = RT \ln \left(\frac{f_i}{y_i p} \right)$$

$$\text{as } \mu_i = \overline{G}_i$$

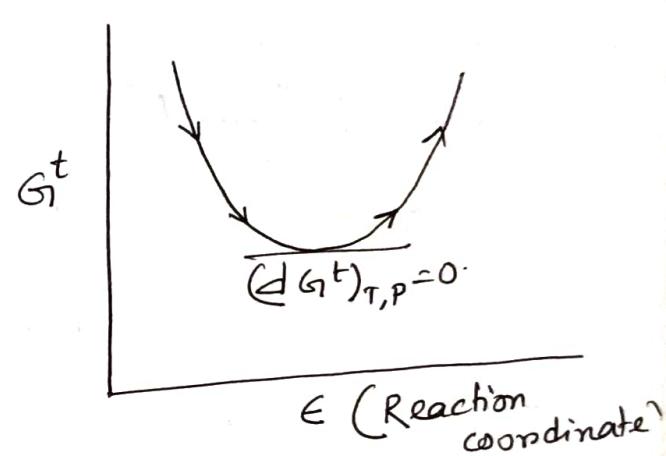
$$\overline{G}_i - \overline{G}_i^{ig} = \overline{G}_i^R = RT \ln \hat{\phi}_i$$

Therefore by definition, Fugacity coeff of ith species in solution is given by $\hat{\phi}_i$. It is a dimensionless Ratio.

Chemical Reaction Equilibrium

Equilibrium Criterion:

- The total Gibbs energy of a closed system at const T and P must decrease during an irreversible process.
- The condition for equilibrium is reached when G^t attains its minimum value.
- At this state $(dG^t)_{T,P} = 0$.
- ϵ called the reaction coordinate characterizes the extent or degree to which a reaction has taken place.
- The criteria for Equilibrium are.
 - The total Gibbs free energy is at minimum
 - Its differential at const T and P is zero.



The standard Gibbs free Energy change and the Equilibrium Constant:

Total differential of the Gibbs energy

$$d(G^t) = nVdP - nsdT + \sum \nu_i d\mu_i$$

If a change in the mole number n_i occurs as a result of a single chemical reaction in a closed system, each $d\mu_i$ may replaced by $\nu_i dE$.

Thus the above equation becomes

$$d(nG) = nv dP - nsdT + \sum v_i \mu_i d\epsilon \quad \dots (i)$$

As nG is a state function the right side of the equation (i) is an exact differential expression

Hence,

$$\sum v_i \mu_i = \left[\frac{\partial(nG)}{\partial \epsilon} \right]_{T,P} = \left[\frac{\partial G^t}{\partial \epsilon} \right]_{T,P} \quad \dots (ii)$$

Thus the quantity $\sum v_i \mu_i$ represents the Rate of change of total Gibbs free energy of the system with respect to reaction coordinate at const T and P.

Thus at Equilibrium $\boxed{\sum v_i \mu_i = 0} \quad \dots (iii)$

This becomes a criterion for Equilibrium.

By definition the fugacity of a species in solution is given by

$$\boxed{\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i}$$

For pure species i in its standard state at the same temp and Press is given by

$$G_i = \Gamma_i(T) + RT \ln f_i$$

$$\therefore \mu_i - G_i = RT \ln \left(\frac{\hat{f}_i}{f_i} \right)$$

From eqn (iii)

$$\sum v_i \left(G_i + RT \ln \frac{\hat{f}_i}{f_i} \right) = 0$$

$$\sum v_i G_i + \sum RT v_i \ln \frac{\hat{f}_i}{f_i} = 0$$

$$\sum v_i G_i = - RT \sum \ln \left(\frac{\hat{f}_i}{f_i} \right)^{v_i}$$

$$-\frac{\sum v_i G_i}{RT} = \ln \prod_i \left(\frac{\hat{f}_i}{f_i} \right)^{v_i}$$

[as we are inserting summation in the ln that's why]

In exponential form, This eqn becomes, summation becomes multiplication \prod

$$\prod_i \left(\frac{\hat{f}_i}{f_i} \right)^{v_i} = K \quad (\text{by definition}).$$

$$\text{where } K = \exp \left(-\frac{\Delta G^\circ}{RT} \right)$$

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

$$\text{as by definition } \Delta G^\circ = \sum_i v_i G_i^\circ$$

Because G_i° is a property of pure species i in its standard state at fixed pressure, it depends only on temperature.

Despite its dependence on temp, K is called the equilibrium constant for the reaction ΔG° is called the std Gibbs energy change of reaction.

The function $\Delta G^\circ = \sum v_i G_i^\circ$ is the difference between the Gibbs energies of the products and reactants when each is in its std state as a pure substance at the std state pressure but at the system temp.

Thus the value of ΔG° is fixed for a given reaction once the temp is established and it is independent of pressure and composition.

Thus for general property M.

$$\Delta M^\circ = \sum \nu_i M_i^\circ$$

$$\therefore H_i^\circ = -RT^2 \frac{d C_p^\circ}{dT}$$

$$\sum_i \nu_i H_i^\circ = -RT^2 d \left(\sum_i \frac{\nu_i C_p^\circ}{RT} \right) \frac{dT}{dT}$$

$$\Delta H^\circ = -RT^2 \frac{d \left(\frac{\Delta C_p^\circ}{RT} \right)}{dT}$$

Effect of Temperature on the Equilibrium constant :-

Because the std-state temp ... is that of the equilibrium mixture, the std property changes of Rxn, such as ΔC_i° and ΔH° vary with the equilibrium temp.

The dependence of ΔC_i° on T is given by

$$\frac{d \left(\frac{\Delta C_i^\circ}{RT} \right)}{dT} = -\frac{\Delta H^\circ}{RT^2}$$

$$-\frac{d(\ln K)}{dT} = -\frac{\Delta H^\circ}{RT^2}$$

ΔH° = standard enthalpy change of the reaction.
it is independent of T

$$\ln \left(\frac{K}{K'} \right) = -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

$$\ln \left(\frac{K}{K'} \right) = \frac{\Delta H}{R} \left(\frac{1}{T'} - \frac{1}{T} \right)$$

Multiplying v_i and summing overall species

$$d(\sum v_i s_i^\circ) = \sum v_i c_p^\circ \frac{dT}{T}$$

$$d(\Delta S^\circ) = \Delta c_p^\circ \frac{dT}{T}$$

$$\text{or } \int_{\Delta S_0}^{\Delta S^\circ} d(\Delta S') = \int_{T_0}^T \Delta c_p^\circ \frac{dT}{T}$$

$$\Delta S_0 = \Delta S^\circ + R \int_{T_0}^T \frac{\Delta c_p^\circ}{R} \frac{dT}{T} \quad \dots \dots \dots (i)$$

$$\text{Now } \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta c_p^\circ}{R} dT - T \left(\Delta S_0 + R \int_{T_0}^T \frac{c_p^\circ}{R} \frac{dT}{T} \right)$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta c_p^\circ}{R} dT - T \Delta S_0 - RT \int_{T_0}^T \frac{c_p^\circ}{R} \frac{dT}{T}$$

To eliminate ΔS_0 from this equation,

$$\Delta S_0 = \frac{\Delta H_0^\circ - \Delta G_0^\circ}{T_0}$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta c_p^\circ}{R} dT$$

$$\text{We know } G_i^\circ = H_i^\circ - TS_i^\circ$$

multiplying both side by v_i and summation over all species

$$\sum v_i G_i^\circ = \sum v_i H_i^\circ - T \sum v_i S_i^\circ$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

The standard heat of reaction is related to temp

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{C_p}{R} dT$$

$$[\text{as } \int_{\Delta H_0^\circ}^{\Delta H^\circ} d\Delta H^\circ = \int_{T_0}^T \Delta C_p^\circ dT]$$

The temperature dependence of the standard entropy change of reaction is developed simultaneously.

The std-state entropy of species i at the constant std state pressure P° is given by

$$dS_i^\circ = C_{p,i}^\circ \frac{dT}{T}$$

Multiplying by v_i - summing over all species

$$d(\sum v_i S_i^\circ) = \sum v_i C_{p,i}^\circ \frac{dT}{T}$$

$$d(\Delta S^\circ) = \Delta C_p^\circ \frac{dT}{T}$$

$$\int_{\Delta S_0^\circ}^{\Delta S^\circ} d(\Delta S^\circ) = \int_{T_0}^T \Delta C_p^\circ \frac{dT}{T}$$

$$\boxed{\Delta S^\circ = \Delta S_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}}$$

$$\text{Now, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT - T \left(\Delta S_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T} \right)$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT - T\Delta S_0^\circ - RT \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

To eliminate ΔS_0° from the equation through the relationship

$$\Delta S_0^\circ = \frac{\Delta H_0^\circ - \Delta G_0^\circ}{T_0}$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT - \frac{T}{T_0} (\Delta H_0^\circ - \Delta G_0^\circ) - RT \int_{T_0}^T \frac{\Delta C_p^\circ}{R} \frac{dT}{T}$$

Dividing by RT on both sides we get,

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta H_0^\circ}{RT} + \frac{(\Delta G_0^\circ - \Delta H_0^\circ)}{RT_0} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^\circ dT}{R} - \int_{T_0}^T \frac{\Delta C_p^\circ dT}{RT}$$

Sample Questions

- 1) Derive an expression for chemical potential of species i in the mixture from fundamental property relation.
- => The total Gibbs free energy of any closed system is given by,

$$d(n\mathcal{G}) = (nV)dP - (nS)dT$$

where n is the total no of moles in the system
This equation is applicable for single phase closed system where no chemical reaction occurs.

For a single phase open system material may pass in and out of the system, and $n\mathcal{G}$ becomes a function of n .

$$\text{Thus } n\mathcal{G} = f(P, T, n_1, n_2, \dots, n_i, \dots)$$

The total differential of $n\mathcal{G}$

$$d(n\mathcal{G}) = \left(\frac{\partial n\mathcal{G}}{\partial T}\right)_{P,n} dT + \left(\frac{\partial n\mathcal{G}}{\partial P}\right)_{T,n} dP + \sum_i \left(\frac{\partial n\mathcal{G}}{\partial n_i}\right)_{P,T,n_j} dn_i$$

The summation is over all species present and subscript n_j indicates that all mole number except the i^{th} are held const.

The chemical potential of i^{th} species in the mixture,

$$\mu_i = \left[\frac{\partial (n\mathcal{G})}{\partial n_i}\right]_{P,T,n_j}$$

2) What is the criterion for multiphase equilibrium?

⇒ Let two phases α and β they mutually non reacting and each individual phase is open to each other and mass transfer between the phases may occur. Then

$$d(n_G)^\alpha = (nv)^\alpha dP - (ns)^\alpha dT + \sum \mu_i^\alpha dn_i^\alpha \quad \dots (i)$$

and $d(n_G)^\beta = (nv)^\beta dP - (ns)^\beta dT + \sum \mu_i^\beta dn_i^\beta \quad \dots (ii)$

For the system to be in thermal and mechanical equilibrium T and P must be uniform.

The change in total Gibbs energy of the two phase system is the sum of the equation for the separate phases.

$$d(n_G) = d(n_G)^\alpha + d(n_G)^\beta$$

at equilibrium

$$\sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta = 0$$

The changes dn_i^α and dn_i^β result from mass transfer then mass conservation

$$dn_i^\alpha = -dn_i^\beta$$

$$\text{So, } \sum (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

$$\text{Hence } \mu_i^\alpha - \mu_i^\beta = 0 \quad ; \quad \mu_i^\alpha = \mu_i^\beta$$

For multiphase system $\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi$

Thus multiphase system at same T and P are in equilibrium when the chemical potential of each species is same in all phases.

- 3.) Prove that $dM_1/dx_1 = -(x_2/x_1) dM_2/dx_2$

\Rightarrow For a binary solution we can get

$$M = x_1 \bar{M}_1 + x_2 \bar{M}_2 \quad \text{---(i)}$$

$$\text{and } dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2 \quad \text{---(ii)}$$

where M is known as a function of x, at constant T and P.

The appropriate form of the Gibbs Duhem equation is expressed as,

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \quad \text{---(iii)}$$

For binary mixture $x_1 + x_2 = 1$ and $dx_1 = -dx_2$

Putting this in equation (ii)

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 - \bar{M}_2 dx_1$$

$$dM = (x_1 d\bar{M}_1 + x_2 d\bar{M}_2) + (\bar{M}_1 - \bar{M}_2) dx_1$$

$$\frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2$$

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

Thus for binary system the partial properties are readily calculated from the an expression for the solution property as a function of composition at const T and P

The eqn (iii) becomes

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0$$

$$\frac{d\bar{M}_1}{dx_1} = - \frac{x_2}{x_1} \frac{d\bar{M}_2}{dx_1}$$

- 4) The enthalpy of a binary liquid system of species 1 and 2 at fixed temp and pressure is represented by the equation $H = 300x_1 + 450x_2 + x_1x_2(50x_1 + 25x_2)$ where H in J/mol. Determine expressions for partial molar enthalpies of species 1 and 2 as functions of x_1 and numerical values of pure species enthalpy H_1 and H_2 .

\Rightarrow for binary system $x_1 + x_2 = 1$

Putting this in the given equation.

$$\begin{aligned}
 H &= 300x_1 + 450(1-x_1) + x_1(1-x_1)(50x_1 + 25x_2) \\
 &= 300x_1 + 450 - 450x_1 + (x_1 - x_1^2)(50x_1 + 25 - 25x_1) \\
 &= 300x_1 + 450 - 450x_1 + 50x_1^2 + 25x_1 - 25x_1^2 \\
 &\quad - 50x_1^3 - 25x_1^2 + 25x_1^3 \\
 &= 300x_1 - 450x_1 + 25x_1 + 50x_1^2 - 25x_1^2 - 25x_1^2 \\
 &\quad - 50x_1^3 + 25x_1^3 + 450 \\
 &= -125x_1 + 450 - 25x_1^3 \quad \text{--- (i)}
 \end{aligned}$$

$$\text{Now, } \frac{dH}{dx_1} = -125 - 75x_1^2 \quad \dots \text{ (ii)}$$

From the equation of partial properties.

$$\begin{aligned}\bar{H}_1 &= H + x_2 \frac{dH}{dx_1} \\ &= (-125x_1 + 450 - 25x_1^3) + (1-x_1)(-125 - 75x_1^2) \\ &= -125x_1 + 450 - 25x_1^3 - 125 - 75x_1^2 + 125x_1 + 75x_1^3 \\ &= 325 - 75x_1^2 + 50x_1^3 \quad \dots \text{ (iii)}\end{aligned}$$

Again,

$$\begin{aligned}H_2 &= H - x_1 \frac{dH}{dx_1} \\ &= (-125x_1 + 450 - 25x_1^3) - x_1(-125 - 75x_1^2) \\ &= -125x_1 + 450 - 25x_1^3 + 125x_1 + 75x_1^3 \\ &= 450 + 50x_1^3 \quad \dots \text{ (iv)}\end{aligned}$$

Determination of \bar{H}_1 and H_2 :

For calculation of \bar{H}_1 , $\bar{H}_1 = H$,

when $x_1 = 1$ we get

$$H_1 = 325 - 75 + 50 = 300 \text{ J/mol.}$$

From (iv)

$$\bar{H}_2 = H_2 \quad \text{when } x_1 = 0$$

$$H_2 = 450 \text{ J/mol.}$$

Fugacity coefficient :-

The fugacity coeff is a dimensionless quantity that relates the fugacity of real gas to the fugacity of an ideal gas at the same temp and pressure.

It is denoted by $\phi_i = \frac{f_i}{P}$

The fugacity coeff accounts the deviation of a real gas from ideal behavior. For ideal gas $\phi_i = 1$

Chemical Potential :-

The chemical potential of a substance is the amount of energy required to add one mole of the substance to a system while holding the temperature, pressure and composition of the system constant.

It is denoted by $\mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{T, P, n_j}$

Stoichiometric number (γ) :-

The stoichiometric number is the coeff that appears in a balanced chemical equation, indicating the no of moles of a substance that react or are produced in the reaction.



here, a, b, c, d are stoichiometry.

Partial Pressure:

The partial pressure of a gas is the pressure that the gas would exert if it occupied the same volume as the mixture of gases in ~~the~~ which it present, but no other gas were present.

If a mixture contains A and B gas then total pressure

$$P = (\text{partial pressure of A} + \text{partial pressure of B})$$

Phase Rule:

It is a thermodynamic principle that relates the number of degrees of freedom of a system to the number of phases and components presents.

$$F = C - P + 2$$

where F = degrees of freedom

C = no of components

P = no of phases.

Fugacity:

Fugacity is incorporated with non ideal behavior of gas. The fugacity measures the Gibbs energy of a real gas in the same way as the pressure measure the Gibbs energy of an ideal gas.

Reaction co-ordinate:

The reaction co-ordinate is a parameter that describes the progress of a chemical reaction and it is often used to represent the extent of the reaction.

Entropy:

Entropy is a thermodynamic property that measures the degree of randomness or disorder of a system, and it is a measure of the no of ways in which the energy of a system can be distributed.

Gibbs free Energy:

Gibbs free energy is a thermodynamic property that measure the maximum amount of useful work that can be obtained from a system at constant temperature and pressure.

Partial molar Property:

A partial molar property is a thermodynamic property that represents the change in a property of a mixture when an infinitesimal amount of a component is added to the mixture while keeping the temperature, P and composition of the mixture constant.

$$\delta \bar{M}_i = \left(\frac{\partial M}{\partial n_i} \right)_{T, P, n_j}$$

Statefunction:

A state function is a property that depends only on the current state of a system and not on the path by which the system arrived at that state.

Ex - internal energy, enthalpy, entropy.

6) The need arises in laboratory of 2000cc of an antifreeze solution consisting of 30 mol% methanol in water. what volumes of pure methanol and of pure water at 25°C must be mixed to form 2000cc of antifreeze also at 25°C? Partial molar volumes for methanol and water in 30 mol% methanol solution and their pure species molar volume both at 25°C are:

$$\text{Methanol : } v_1 = 38.632 \text{ cc/mol}$$

$$v_1 = 40.727 \text{ cc/mol}$$

$$\text{water : } v_2 = 17.76 \text{ cc/mol}$$

$$v_2 = 18.068 \text{ cc/mol.}$$

⇒ For the binary solution the the summability relation is written for molar volume

$$V = x_1 \bar{v}_1 + x_2 \bar{v}_2$$

$$\text{given } x_1 = 0.3 \quad \bar{v}_1 = 38.632 \text{ cc/mol}$$

$$x_2 = 0.7 \quad \bar{v}_2 = 17.765 \text{ cc/mol}$$

$$V = 0.3 \times 38.632 + 0.7 \times 17.765$$

$$= 24.025 \text{ cc/mol.}$$

The total volume required is 2000 cc

$$V^t = nV$$

$$n = \frac{V^t}{V} = \frac{2000}{24.025} = 83.246 \text{ mol}$$

In 83.246 mol 30% is methanol and 70% water

$$n_1 = 0.3 \times 83.246 = 24.974 \text{ mole}$$

$$n_2 = 0.7 \times 83.246 = 58.272 \text{ mole}$$

The volume of each pure species is

$$V_i^t = n_i V_i$$

$$V_1^t = 24.974 \times 40.727 = 1017 \text{ cc}$$

$$V_2^t = 58.272 \times 18.068 = 1053 \text{ cc}$$

7) State the criteria for chemical equilibrium.

⇒ The total Gibbs energy of a closed system at constant T and P decreases during an irreversible process.

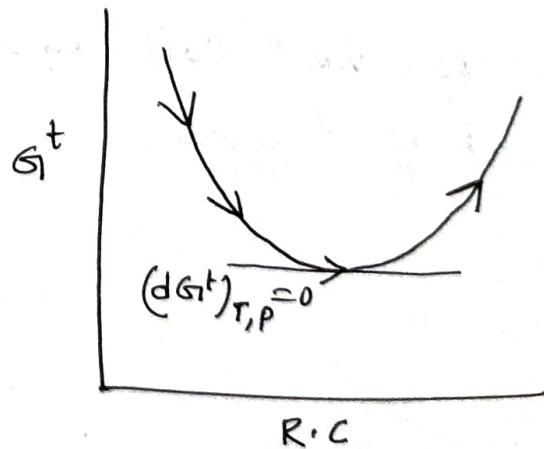
The condition for equilibrium is reached when total Gibbs energy (G^t) attains its minimum value at this equilibrium state

$$(dG^t)_{T,P} = 0$$

The criteria for equilibrium :-

i) The total Gibbs energy G^t is at minimum

ii) Its differential at const T and P is zero.



8) Derive the vant Hoff equation for K_p .

⇒ Considering effect of temperature on equilibrium
The standard Gibbs energy change is expressed as,

$$\Delta G^\circ = -RT \ln K_p$$

$[K_p = \text{rate constant}]$
 $\text{at const } P$

differentiating w.r.t T at const P

$$\left[\frac{\partial \Delta G^\circ}{\partial T} \right]_P = -R \ln K_p - RT \left[\frac{\partial \ln K_p}{\partial T} \right]_P$$

multiplying by T both side

$$T \left[\frac{\partial \Delta G^\circ}{\partial T} \right]_P = -RT \ln K_p - RT^2 \left[\frac{\partial \ln K_p}{\partial T} \right]_P$$

From fundamentals $\left[\frac{\partial \Delta G^\circ}{\partial T} \right]_P = -\Delta S^\circ$

Hence $-T \Delta S^\circ = \Delta G^\circ - RT^2 \left[\frac{\partial \ln K_p}{\partial T} \right]_P$

$$\Delta H^\circ = RT^2 \left[\frac{\partial \ln K_p}{\partial T} \right]$$

$$\boxed{\frac{\Delta H^\circ}{RT^2} = \frac{\partial \ln K_p}{\partial T}}$$

∴ According to Gibbs-Helmholtz eqⁿ

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

This is the vant Hoff equation for K_p . where K_p is independent of pressure.

9) Derive the van't Hoff equation for K_c .

⇒ In order to get vant Hoff equation for K_c we will try to relate K_p with K_c

$$K_p = K_c (RT)^{m n}$$

where $m = \text{stoichiometry of product}$

$$\ln K_p = \ln K_c + m \ln R + m \ln T$$

- stoichiometry of reactant

differentiating w.r.t T at constant P

$$\left(\frac{\partial \ln K_p}{\partial T} \right)_P = \left(\frac{\partial \ln K_c}{\partial T} \right)_P + m \left(\frac{\partial \ln T}{\partial T} \right)_P$$

$$\frac{\Delta H^\circ}{RT^2} = \left(\frac{\partial \ln K_c}{\partial T} \right)_P + \frac{m}{T}$$

$$\frac{\Delta H^\circ}{RT^2} - \frac{m}{T} = \left(\frac{\partial \ln K_c}{\partial T} \right)_P$$

$$\frac{\Delta H^\circ - \Delta n RT}{RT^2} = \left(\frac{\partial \ln K_c}{\partial T} \right)_P \quad \dots \text{(i)}$$

Again $\Delta H^\circ = \Delta U^\circ + \Delta PV$
 $= \Delta U^\circ + P \Delta V$ at constant Pressure.

From equation (i)

$$\frac{\Delta H^\circ - P \Delta V}{RT^2} = \left(\frac{\partial \ln K_c}{\partial T} \right)_P$$

$$\frac{\Delta U^\circ + P \Delta V - P \Delta V}{RT^2} = \left(\frac{\partial \ln K_c}{\partial T} \right)_P$$

$$\boxed{\frac{\Delta U^\circ}{RT^2} = \left(\frac{\partial \ln K_c}{\partial T} \right)_P}$$

10) Prove that an increase in temperature should favour endothermic reactions.

→ Endothermic reactions are those that absorb energy from their surroundings in the form of heat.

We can simply say the change of enthalpy for an endothermic process is negative.

Now according to vant Hoff equation

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

on integration we get.

$$\frac{K_p_2}{K_p_1} \int d \ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln\left(\frac{K_p_2}{K_p_1}\right) = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

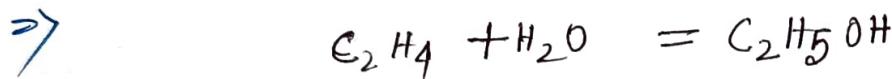
This equation indicates that if $T_1 < T_2$ the R.H.S of the equation will be +ve or $K_p_2 > K_p_1$, provided ΔH is also +ve (The reaction is endothermic)

This is in agreement with Le Chatelier's principle according to which an increase in temp should favour endothermic reactions.

12) calculate the equilibrium constant for vapour phase hydration of ethylene at 145°C and 320°C

	A	B $\times 10^3$	C $\times 10^6$	D $\times 10^{-5}$	$\Delta H_{298}^\circ \text{ J/mol}$	$\Delta G_{298}^\circ \text{ J/mol}$
$\text{C}_2\text{H}_5\text{OH}$	3.518	20.001	-6.002	0	-235.100	-168.490
C_2H_4	1.424	14.394	-4.392	0	52.510	68.460
H_2O	3.47	1.45	0	0.121	-241.818	-2281572

Given: $\frac{\Delta C_P}{R} = \Delta A + \Delta B T + \Delta C T^2 + \Delta D T^{-2}$



$$\Delta B = \Delta B_{\text{C}_2\text{H}_5\text{OH}} - (\Delta B_{\text{H}_2\text{O}} + \Delta B_{\text{C}_2\text{H}_4})$$

$$\Delta B \times 10^3 = 20.001 - (14.394 + 1.45)$$

$$\Delta B = 4.157 \times 10^{-3}$$

$$\begin{aligned}\Delta A &= 3.518 - (1.424 + 3.47) \\ &= -1.376\end{aligned}$$

$$\begin{aligned}\Delta C &= [-6.002 - (-4.392 + 0)] \times 10^{-6} \\ &= -1.61 \times 10^{-6}\end{aligned}$$

$$\begin{aligned}\Delta D &= [0 - (0 + 0.121)] \times 10^5 \\ &= -0.121 \times 10^5\end{aligned}$$

$$\begin{aligned}\Delta H^\circ &= -235.100 - (52.510 - 241.818) \\ &= -45.792 \text{ J/mol}\end{aligned}$$

$$\Delta G^\circ = -8378 \text{ J/mol.}$$

From vant Hoff equation.

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

$$\ln \frac{K_{P_2}}{K_{P_1}} = \int_{298}^{418} \frac{\Delta H^\circ_{298}}{RT^2} dT + \int_{298}^{418} \frac{1}{RT^2} \left[\int_{R}^{C_P} dT \right] dT$$

$$\ln \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H^\circ_{298}}{R} \left[\frac{1}{298} - \frac{1}{418} \right] + \int_{298}^{418} \frac{1}{T^2} \left[\Delta A(418 - 298) + \frac{\Delta B}{2} (418^2 - 298^2) \right. \\ \left. + \frac{\Delta C}{3} (418^3 - 298^3) + \Delta D \left(\frac{1}{298} - \frac{1}{418} \right) \right] dT$$

~~$$= -5.3 - 1.376 \times 120 \int_{298}^{418} \frac{dT}{T^2} + \frac{4.157 \times 10^3}{2} \times$$~~

$$= -5.3 + \int_{298}^{418} \left(-1.376 \times 120 + \frac{4.157 \times 10^3}{2} \times 85920 - \frac{1.61 \times 10^{-6}}{3} \times 46.57 \times 10^6 \right. \\ \left. + 0.121 \times 9.63 \times 10^{-4} \times 10^5 \right) \frac{dT}{T^2}$$

$$= -5.3 + \int_{298}^{418} \left(-165.12 + 178.58 - 24.99 - 11.6 \right) \frac{dT}{T^2}$$

$$= -5.3 - \left\{ 11.52 \times \left(\frac{1}{298} - \frac{1}{418} \right) \right\}$$

$$= -5.3 - 0.022$$

$$= -5.322$$

$$\Delta G^\circ = -RT \ln K_{P_{298}} ; \ln K_{P_{298}} = \frac{8378}{8.318 \times 298}$$

$$K_{P_1} \text{ or } K_P = 29.41$$

Again $\ln \frac{K_{P_2}}{K_{P_1}} = -5.322$

$$K_{P_2} = e^{-5.322} \times 29.41 \\ = 0.1436$$

Now for 320°C or 593K .

$$\begin{aligned} \ln \frac{K_{P_2}}{K_{P_1}} &= \frac{\Delta H^\circ_{298}}{R} \left[\frac{1}{298} - \frac{1}{593} \right] + \int_{298}^{593} \frac{1}{T^2} \left(\int C_p / R dT \right) dT \\ &= -9.19 + \int_{298}^{593} \frac{1}{T^2} \left[\Delta A (593 - 298) + \frac{\Delta B}{2} (593^2 - 298^2) \right. \\ &\quad \left. + \frac{\Delta C}{3} (593^3 - 298^3) + \Delta D \left(\frac{1}{298} - \frac{1}{593} \right) \right] dT \\ &= -9.19 + \left(-1.376 \times 295 + \frac{4.157 \times 10^{-3}}{2} \times 262845 \right. \\ &\quad \left. - \frac{1.61 \times 10^{-6}}{3} \times 182 \times 10^6 \right. \\ &\quad \left. - 0.121 \times 166.93 \right) \int_{298}^{593} \frac{dT}{T^2} \\ &= -9.19 + (-405.92 + 546.32 - 97.67 \\ &\quad - 20.19) \times \left(\frac{1}{298} - \frac{1}{593} \right) \end{aligned}$$

$$= -9.19 + 0.037$$

$$= -9.15$$

$$\ln \frac{K_{P_2}}{K_{P_1}} = -9.15$$

$$K_{P_2} = e^{-9.15} \times 29.41 \\ = 3.11 \times 10^{-3}$$

Zeroth Law of Thermodynamics

The law states that if two bodies A and B separated by thermal insulator but A and B remain separately connected by to another body C then A and B will be in thermal equilibrium condition when Both A and B remain separately in thermal equilibrium with C.

Solution thermodynamics - Sample Questions:

- 1) The water gas shift reaction. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ is carried out under several sets of conditions described below. Calculate the fraction of steam reacted in each case. Assume the mixture behaves as an ideal gas.
- a) The reactants consists of 1 mol of H_2O vapour and 1 mol of CO. The temperature is 1100K and the pressure is 1 bar. ($1 \text{ bar} = 10^5 \text{ Pa}$, ~~1 bar = 1.01325 bar = 1 atm~~)
 - b) Same as (a) except the pressure is 10 bar
 - c) Same as (a) except that 2 mols of N_2 is included in the reacⁿ.
 - d) The reactants are 2 mol of H_2O and 1 mol of CO. Other condition are same as (a)
 - e) The reactants are 1 mol H_2O and 2 mols of CO. Others same.
 - f) The initial mixture consist of 1 mol of H_2O , 1 mol of CO and 1 mol of CO_2 . Other conditions are same as (a)
 - g) Same as (a) except the temperature is 1650K.

From the graph of $\ln K$ vs $\frac{10^4}{T}$, $\ln K = 0$ or $K = 1$

For the reaction $\sum_i \nu_i = 1 + 1 - 1 - 1 = 0 = \nu$

The reaction mixture can be treated as an ideal gas.

$$\prod_i (y_i)^{\nu_i} = \left(\frac{P}{P_0}\right)^{-\nu} K \quad \dots \dots \text{(i)}$$

or $\frac{y_{H_2} y_{CO_2}}{y_{CO} y_{H_2O}} = \left(\frac{1}{1}\right)^0 \cdot K = 1 \quad \dots \dots \text{(ii)}$

By equation (i), $y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i e}{n_0 + \nu e}$ at equilibrium.

$$y_{CO} = \frac{1 - e_e}{2} \quad \text{at equilibrium} \quad \dots \dots \text{(iii)}$$

$$y_{H_2O} = \frac{1 - e_e}{2} \quad \dots \dots \text{(iv)}$$

$$y_{CO_2} = \frac{0 + e_e}{2} = \frac{e_e}{2} \quad \dots \dots \text{(v)}$$

$$y_{H_2} = \frac{0 + e_e}{2} = \frac{e_e}{2} \quad \dots \dots \text{(vi)}$$

putting (iii), (iv), (v), (vi) in (ii)

$$\left[\frac{\left(\frac{1 - e_e}{2}\right)^2}{\left(\frac{e_e}{2}\right)^2} \right]^{-1} = 1$$

$$\frac{1 + e_e^2 - 2e_e}{4} = \frac{e_e^2}{4}$$

$$e_e = \frac{1}{2} = 0.5$$

a) 50% steam has been reacted on the fraction of steam reacted is 0.5.

b) Because $\gamma = 0$ $(P/P_0)^{-\gamma}$ does not have any effect on the ideal gas reaction, i.e. increase in pressure does not have any effect.

c) 2 mol of N_2 is added. N_2 does not take part in reaction and serves only as a diluent.

It only increases the initial no of moles no from 2 to 4. and the mole fraction are all reduced by a factor 2.

$$y_{CO} = \frac{1 - \epsilon_e}{4}$$

$$y_{H_2O} = \frac{1 - \epsilon_e}{4}$$

$$y_{CO_2} = \frac{\epsilon_e}{4}$$

$$y_{H_2} = \frac{\epsilon_e}{4}$$

$$\frac{y_{H_2} \cdot y_{CO_2}}{y_{H_2O} y_{CO_2}} = K = \left[\frac{(1 - \epsilon_e)/4}{(\epsilon_e/4)^2} \right] - 1$$

$$\epsilon_e = 0.5$$

Hence the fraction of steam reacted is same.

d) 2 mol H_2O and 1 mol CO_2

$$n_0 = 3 \text{ mol}$$

$$y_{CO} = \frac{n_{CO_0} - \gamma_i \epsilon_e}{n_0} = \frac{1 - \epsilon_e}{3}$$

$$y_{H_2O} = \frac{2 - \epsilon_e}{3}$$

$$y_{CO_2} = \frac{0 + \epsilon_e}{3} = \frac{\epsilon_e}{3}$$

$$y_{H_2} = \frac{\epsilon_e}{3}$$

At equilibrium ,

$$\frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = K$$

or, $\frac{\left(\frac{\epsilon_e}{3}\right)^2}{\left(\frac{1-\epsilon_e}{3}\right) \left(\frac{2-\epsilon_e}{3}\right)} = 1$

or, $\frac{\epsilon_e^2}{(1-\epsilon_e)(2-\epsilon_e)} = 1$

$$\epsilon_e = \frac{2}{3} = 0.667.$$

e) 1 mol H_2O and 2 mol CO

$$y_{CO} = \frac{2-\epsilon_e}{3} \quad y_{H_2O} = \frac{1-\epsilon_e}{3} \quad y_{CO_2} = \frac{\epsilon_e}{3} \quad y_{H_2} = \frac{\epsilon_e}{3}$$

$$\frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = K \quad \text{Ans.}$$

or, $\frac{\left(\frac{\epsilon_e}{3}\right)^2}{\left(\frac{2-\epsilon_e}{3}\right) \left(\frac{1-\epsilon_e}{3}\right)} = 1$

$$\epsilon_e^2 = 2 - 3\epsilon_e + \epsilon_e^2 \quad \text{Ans}$$

$$\epsilon_e = \frac{2}{3} = 0.667$$

f) 1 mol H_2O and 1 mol CO and 1 mol CO_2

$$n_0 = 3 \text{ mol}$$

$$y_{CO} = \frac{1-\epsilon_e}{3} \quad y_{CO_2} = \frac{1+\epsilon_e}{3}$$

$$y_{H_2O} = \frac{1-\epsilon_e}{3} \quad y_{H_2} = \frac{\epsilon_e}{3}$$

At equilibrium,

$$\frac{y_{CO_2} \cdot y_{H_2}}{y_{CO} \cdot y_{H_2O}} = K$$

$$\frac{\frac{(1+\epsilon_e)}{3} \times \frac{(\epsilon_e)}{3}}{\left(\frac{1-\epsilon_e}{3}\right)^2} = 1$$

$$\epsilon_e + \cancel{\epsilon_e} = 1 + \cancel{\epsilon_e} - 2\epsilon_e.$$

$$\epsilon_e = \frac{1}{3} = 0.33$$

2) At 1680K from $\ln K$ vs $\frac{10^3}{T}$ graph $\ln K = -1.15$
on $K = 0.316$

$$y_{CO} = \frac{1-\epsilon_e}{2} \quad y_{CO_2} = \frac{\epsilon_e}{2}$$

$$y_{H_2O} = \frac{1-\epsilon_e}{2} \quad y_{H_2} = \frac{\epsilon_e}{2}$$

at equilibrium,

$$\frac{y_{H_2} y_{CO_2}}{y_{H_2O} y_{CO}} = 0.316$$

$$\frac{\left(\frac{\epsilon_e}{2}\right)^2}{\left(\frac{1-\epsilon_e}{2}\right)^2} = 0.316$$

$$\frac{\epsilon_e^2}{(1-\epsilon_e)^2} = 0.316$$

$$\epsilon_e^2 = (1 + \epsilon_e^2 - 2\epsilon_e) \times 0.316$$

$$\epsilon_e^2 - 0.316\epsilon_e^2 = 0.316 - 0.632\epsilon_e$$

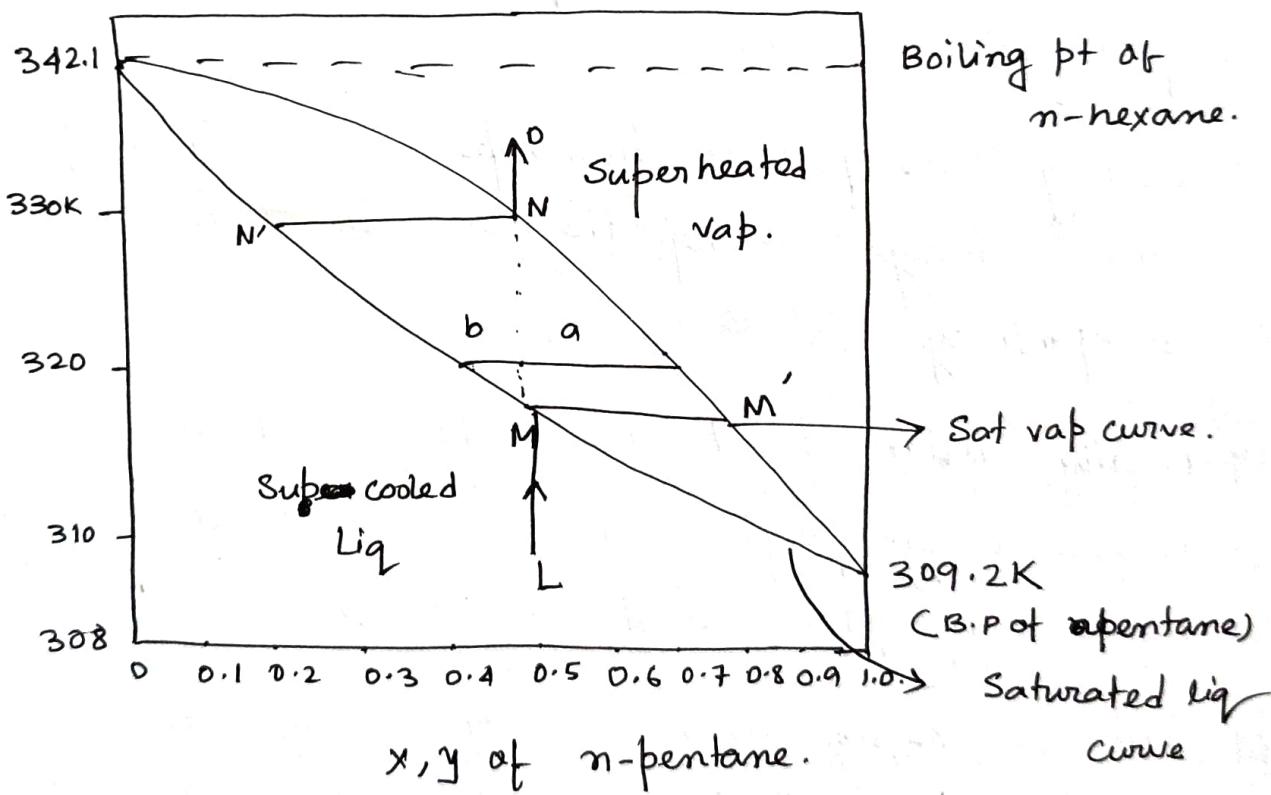
$$0.684 \epsilon_e^2 + 0.632 \epsilon_e - 0.316 = 0$$

$$\epsilon_e = \frac{-0.632 \pm \sqrt{(0.632)^2 - 4 \times 0.684 \times (-0.316)}}{2 \times 0.684}$$

$$\epsilon_e = 0.36$$

The reaction is exothermic and the extent of the reaction decreases with increasing temperature.

- 2) What is VLE? Explain the concept of VLE with the help of a T-x-y curve for a binary mixture.



VLE means vapour-liquid equilibrium.

When a liquid mixture is heated from a subcooled state at constant pressure, the vaporization occurs over a range of temperature unlike vaporization of a pure substance which occurs at const temp at a given pressure.

- For any mixture the two limiting temperatures of the above range are known as bubble point and dew point.
- When the mixture is heated from point L the mixture temperature follows path LM.
- At M, the liquid mixture is saturated and a slight increase in temperature will form a bubble of vapour. Hence the point M is called bubble point.
- As the heating process is continuous beyond M, the temp rises, the amount of vapour increases and the amount of liquid decreases.
- During this process the vapour and liquid phase compositions changes along the ~~the~~ path M'N and MN' respectively.
- Finally at the point N is approached the liquid phase is completely vaporized to a saturated vapour phase. Hence point N is called dew point.
- Further heating above point N increases the temperature of the vapour phase and the vapour gets super heated.
- When a vapour-Liquid mixture is present amount of both phase can be calculated by tie-line method.

A ~~horizontal~~ horizontal line at Q is the tie line.

$$\frac{\text{Amt of liquid mixture}}{\text{Amt of vap mixture}} = \frac{a}{b}$$

State of vapour- liquid mixtures.

<u>Condition</u>	<u>State of mixture</u>
$T < T_{BB}$	Subcooled liq mixture.
$T = T_{BB}$	Saturated liq mixture.
$T_{BB} < T < T_{DP}$	Equilibrium vapour liquid mixture.
$T = D_p$	Saturated vapour mixture
$T > D_p$	Super heated vapour mixture

3) State Dehem's theorem and phase rule.

o) The number of variables that are independently fixed in a system at equilibrium is the difference between the total number of variable that characterize the intensive state of the system and the no of independent equations that can be written relating those variables.

The intensive state of a PVT system containing N chemical species and π phases in equilibrium is characterized by its temp (T), Pressure (P), and $(N-1)$ mole fractions for each phase.

The NO of these phase rule variables
= $2 + (N-1)\pi$

The no of independent phase-equilibrium equation is.
 $(\pi-1)N$

∴ Degrees of freedom, of the system

$$F = [2 + (N-1)\pi] - [(\pi-1)N]$$

$$\boxed{F = N-\pi+2}$$

This is called the phase rule.

Douhem's Theorem :-

This is another rule similar to the phase rule that applies to the extensive state of a closed system at equilibrium.

When both the extensive state and intensive state of the system are fixed the state of the system is said to be completely determined.

It is characterized not only by the $2 + (N-1)\pi$ intensive variables but also by the π extensive variables represented by the mole number of the phases.

Thus the total no of variable is

$$2 + (N-1)\pi + \pi = 2 + N\pi$$

For a closed system formed from specified amount of the chemical species present, a material balance equation can be written for each of the N chemical species, providing N more equations.

These in addition to the $(\pi-1)N$ phase-equilibrium equations, represent a number of independent equations equal to

$$(\pi-1)N + N = N\pi$$

The difference between no of variable and no of equations are,

$$2 + N\pi - N\pi = 2$$

On the basis of this result Duhem's theorem is stated as follows:

For any closed system formed from known amount of prescribed species the equilibrium state is completely determined when any two independent variables are fixed. The two variables may be intensive or extensive.

However the number of independent intensive variables is given by the phase rule.

Thus when $F=1$ at least one of the two variable must be extensive.

When $F=0$ both the independent variables are extensive.