CHEMICAL ENGINEERING (GATE & PSUs)

Postal Correspondence

STUDY MATERIAL (Handwritten Notes)

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Solution Thermodynamics

GATE-2022 Syllabus: Chemical Engineering

First and Second laws of thermodynamics. Applications of first law to close and open systems. Second law and Entropy. Thermodynamic properties of pure substances: Equation of State and residual properties, properties of mixtures: partial molar properties, fugacity, excess properties and activity coefficients; phase equilibria: predicting VLE of systems; chemical reaction equilibrium.

SOLUTION THERMODYNMAICS COURSE CONTENT

1. **Introduction**
2. **Phase Rule & VLE**
3. **Equation of State and residual properties and properties of mixtures**
   - **Partial molar properties**
   - **fugacity**
   - **excess properties and**
   - **activity coefficients**
4. **Phase equilibria**
   - Predicting VLE of systems
   - Chemical reaction equilibrium.

<u>Note for Student:</u>

1. Full GATE Syllabus covers in Notes.

2. Total number of pages in Thermo-II Notes = 190 Pages

3. No. of Questions solved in Notes = 75+ Questions

(GATE PYQs & other good quality question)

VAPOR / LIQUID EQUILIBRIUM (V-L-E)

→ processes such as distillation, Absorption and Extraction bring phases of different composition into contact, and when the phases are not in equilibrium, mass transfer between the phases altere their compositions. Both the extent of change and the rate of transfer depend on the departure of the system from equilibrium.

→ The VLE operation considered the interphase transfer of Mass and energy which result when a gas is brought into contact with a pure liquid in which it is essentially insoluble.

Nature of Equilibrium :→

→ Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time.

→ This implies a balance of all potentials that may cause change.

Example → In the Reboiler for a distillation column, equilibrium b/w vapour and liquid phases is assumed.

→ An isolated system consisting of liquid and vapour phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the system. The temperature, pressure, and phase compositions reach final values which thereafter remain fixed. The system is in equilibrium.

Measures of composition ⇒

Mass fraction, Mole fraction and Molar concentration

1) Mass fraction = $\dfrac{\text{mass of a particular chemical species in a mixture or solution}}{\text{Total mass of the mixture or solution}}$

$$x_i = \frac{m_i}{m}$$

2) Mole fraction = $\dfrac{\text{Number of moles of a particular chemical species in a mixture or solution}}{\text{Total number of moles of the mixture or solution}}$

$$x_i = \frac{n_i}{n}$$

3) Molar concentration = $\dfrac{\text{mole fraction of a particular chemical species in a mixture or solution}}{\text{Molar volume}}$

$$C_i = \frac{x_i}{V}$$

* for flow process

$$X_i = \frac{\dot{m}_i}{\dot{m}} \quad ; \quad x_i = \frac{\dot{n}_i}{\dot{n}} \quad ; \quad C_i = \frac{\dot{n}_i}{q}$$

$\dot{m}_i$ = Mass flow rate of species i

$\dot{n}_i$ = Molar flow rate of species i

q = volumetric flow rate (m^3/sec)

* Molar Mass of a mixture or solution :- (The mole-fraction weighted sum of the molar masses of all species present)

$$M = \sum_i x_i M_i$$

1) Raoult's Law :- (Ideal-Gas & Ideal Solution)

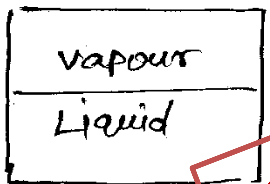
* Assumption required to reduce VLE calculation to Raoult's Law are :-

I) The vapor phase is an ideal gas which means it applicable only for low to moderate pressure.

II) The liquid phase is an ideal solution which means . it implies that it can have approximate validity only when the species are chemical similar. (chemical compositions are same)

At equilibrium

VLE



Raoult's Law

$$y_i P = x_i P_i^{sat} \quad (i = 1, 2 \cdot \cdot N)$$

Where x_i = Liquid-phase mole fraction

y_i = vapor phase mole fraction.

P_i^{sat} = vapor-pressure of pure species i at the temperature of system.

P = total pressure of system

$$\bar{P}_i = y_i P = x_i P_i^{sat}$$

$\bar{P}_i = y_i P$ = Partial pressure of species i.

* Real gas as a Ideal gas → { * At High T, * At Low P }

→ Ideal-solution behavior is often approximated by liquid phases wherein the molecular species are not too different in size and are of the same chemical nature.

Thus, a mixture of isomers, such a ortho; meta- and para-xylene, conforms very closely to ideal-solution behavior. (mixtures of adjacent members of a ~~Homogo~~ Homologoue series).

Example:- n-hexane - n-heptane, ethanol/propanol, benzene/toluene, acetone/acetonitrile and acetonitrile/nitromethane.

* Limitation of Raoult's Law :-

→ It can be applied only to species for which a vapor pressure is known, and this requires that the species be "subcritical" (i.e that the temperature of application be below the critical temperature of the species).

2) Henry's Law :-

Henry's Law states that the partial-pressure of the species in the vapour phase is directly proportional to its liquid-phase mole fraction.

thus

$$\bar{P_i} = y_i P \propto x_i$$

valid only
- 1) At VLE
- 2) Diluted solution
- 3) At low pressure

$$\boxed{\bar{P_i} = y_i P = H_i x_i}$$

Where H_i = Henry's constant (experimental terms).

P_i = partial pressure of species i

* Henry's Law :- (P_i^{sat} = partial pressure)

→ Application of Raoult's law to species i requires a value for P_i^{sat} at the temperature of application, and thus is not appropriate for a species whose critical temperature is less than the temperature of application.

"Henry's law states that the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction"

partial pressure $\boxed{y_i P = x_i H_i}$

↳ Henry's Law for a species present as a very dilute solute in the liquid phase.

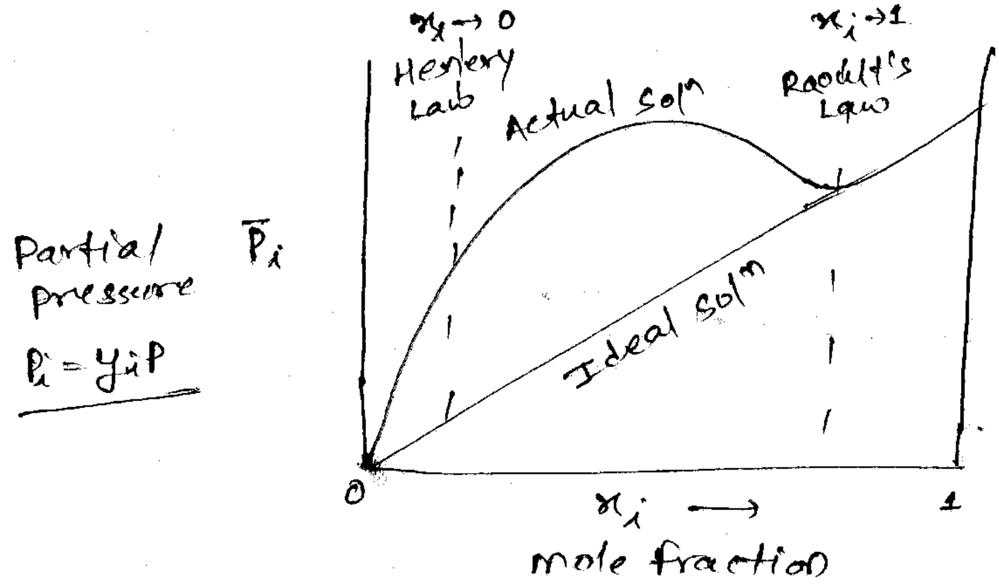
Example - If a system of air in contact with liquid water is presumed at equilibrium, then the air is saturated with water.

→ The mole fraction of water vapor in the air is usually found from Raoult's law applied to the water with the assumption that no air dissolves in the liquid phase. Thus, the liquid water is regarded as pure and Raoult's law for the water (species) becomes

$$y_2 P = x_2 P_2^{sat} \quad \text{put } x_2 = 1$$

$$\boxed{y_2 P = P_2^{sat}} \Rightarrow y_2 = P_2^{sat}/P$$

→ The mole fraction of air dissolved in the water is found from Henry's law. because the critical temperature of air is much lower than 25°C (298.15).



3) Modified Raoult's Law ⇒

For Law to moderate pressure a much more realistic equation for VLE results when the second major Raoult's - Law assumption (Liquid phase is an ideal solution) is abandoned, and account is taken of deviations from solution ideality in the liquid phase by a factor inserted into Raoult's Law, modified to real

$$y_i P = \gamma_i x_i P_i^{sat}$$

Where γ_i = Activity coefficient

x_i = Liquid phase mole fraction

y_i = vapour phase mole fraction

P = total pressure

P_i^{sat} = vapour pressure of pure species i at the temperature of system

* $\gamma_i = f$ (temp & liquid - phase composition)

Different Models are available to find the value of Activity coefficient (γ) :- [for Binary solution]

1) Van-Laar equation ****
2) Margules equation ****
3) Wohl's equation

* 1) Van-Laar Equation :-

$$\left\{ \begin{aligned} A &= \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right]^2 \\ B &= \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2 \end{aligned} \right\}$$

Where A & B are van-Laar coefficient / constant and independent of composition.

*2) Margules equation :

(A=B)

(I) Margules two suffix equation [A & x_1 or x_2]

$$\ln \gamma_1 = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

(II) Margules three suffix equation [A, B & (x_1 or x_2)]

$$\left\{ \begin{aligned} \ln \gamma_1 &= x_2^2 \left[A + 2(B-A) x_1 \right] \\ \ln \gamma_2 &= x_1^2 \left[B + 2(A-B) x_2 \right] \end{aligned} \right\}$$

→ • A, B are margules constant & independent of composition

Que→118) A binary liquid mixture of A and B contains 20 mol% A. At 350 K the vapour pressure of pure A and pure B are 92 kPa and 35 kPa respectively. The mixture follows Raoult's law. The equilibrium vapour phase mole fraction of 'A' in contact with it liquid mixture at 350 K is ______.

(GATE 2016)

Sol→ Raoult's law $\boxed{y_i P = x_i P_i^{sat}}$

$P = P_1 + P_2$ total pressure $\boxed{P = x_1 P_1^{sat} + x_2 P_2^{sat}}$

$x_1 = 0.2,\ P_1 = 92$ kPa

$x_2 = 0.8,\ P_2 = 35$ kPa

$P = (0.2 \times 92 + 0.8 \times 35)$ kPa

$P = 46.4$ kPa

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{0.2 \times 92}{46.4}$$

$\boxed{y_1 = [illegible]}$ vapour phase mole fraction of A in mixture, Answer

Que→119) An equimolar liquid mixture of species ① & ② is in equilibrium with its vapour at 400 K. At this temp. the vapour pressure of the species are $P_1^{sat} = 180$ kPa & $P_2^{sat} = 120$ kPa. Assuming Raoult's law is valid. The value of y is

(GATE 2010)

(A) 0.3 (B) 0.41 (C) 0.5 (D) 0.6

Sol→ $x_1 = y_2 = 0.5$, $P_1^{sat} = 180$ kPa, $P_2^{sat} = 120$

$P = x_1 P_1^{sat} + x_2 P_2^{sat}$ ⇒ $P = 0.5 \times 180 + 0.5 \times 120$

$P = 150$ kPa

$\boxed{y_i P = x_i P_i^{sat}}$

$$\Rightarrow y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{0.5 \times 180}{150} = 0.6$$

option (D) Answer

Que→12) A binary mixture containing species 1 & 2 forms (GATE 2008) an Azeotrope at 105.4°C and 1.013 bar. The liquid phase mole fraction of component 1 (x_1) of this Azeotrope is 0.62. At 105.4°C the pure component vapour pressure for species 1 & 2 are 0.878 and 0.665 bar. Assume that the vapour phase is an ideal gas mixture. The van-Laar constant A and B are given by the expression.

$$A = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right]^2$$

$$B = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right]^2$$

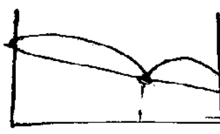
(I) The activity coefficient γ_1 and γ_2 are

(a) (0.88, 0.66) (b) ([illegible], 1.52) (c) (1.52, 1.15) (d) (1.52, 0.88)

(II) The van-Laar constant A & B under these condition are given by

(a) (0.92, 0.87) (b) (1, 1.21) (c) (1.12, 1) (d) (1.52, 1.15)

Sol → (I) * for Azeotrope ($x_i = y_i$)



$$\cancel{y_i} P = \gamma_i \cancel{x_i} P_i^{sat}$$

$$\gamma_i = \frac{P}{P_i^{sat}} \Rightarrow \boxed{\gamma_1 = \frac{P}{P_1^{sat}}, \quad \gamma_2 = \frac{P}{P_2^{sat}}} \text{ at Azeotrope}$$

$x_1 = 0.62$ so $x_2 = 0.38$

$P_1^{sat} = 0.878$ bar

$P_2^{sat} = 0.665$ bar

$P = 1.013$ bar

$$\gamma_1 = \frac{P}{P_1^{sat}} = \frac{1.013}{0.878} = 1.15$$

$$\gamma_2 = \frac{P}{P_2^{sat}} = \frac{1.013}{0.665} = 1.52$$

(1.15, 1.52)

option (b) Answer

(II) van Laar constant A & B

$$\Rightarrow \quad A = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right]^2$$

put $\gamma_1 = 1.15$

$\gamma_2 = 1.52$

$x_1 = 0.62$ & $x_2 = 0.38$

$$A = \ln(1.15) \left[1 + \frac{0.38 \times \ln 1.52}{0.62 \times \ln 1.15} \right]^2$$

$$A = 1.12$$

$$\Rightarrow \quad B = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2$$

$$B = \ln(1.52) \left[1 + \frac{0.62 \ln 1.15}{0.38 \times \ln 1.52} \right]^2$$

$$B \simeq 1$$

(1.12, 1) option (c)

Answer

Ques 124) (GATE 2005) The van Laar Activity coefficient model for a binary mixture is given by

$$\ln \gamma_1 = \frac{A^*}{\left[1 + \frac{A^* x_1}{B^* x_2} \right]^2} \; ; \quad \ln \gamma_2 = \frac{B^*}{\left[1 + \frac{B^* x_2}{A^* x_1} \right]^2}$$

where $\gamma_1 = 1.40$, $\gamma_2 = 1.25$, $x_1 = 0.25$ & $x_2 = 0.75$

Determine constant A^* and B^*

(i) (0.5, 0.3) (ii) (3, 0.5)

(iii) (0.333, 0.2) (iv) (2, 0.333)

Sol → given

(I) method:

$$\ln \gamma_1 = \frac{A^*}{\left(1 + \frac{A^* x_1}{B^* x_2}\right)} \quad ; \quad \ln \gamma_2 = \frac{B^*}{\left(1 + \frac{B^* x_2}{A^* x_1}\right)^2}$$

Where $\gamma_1 = 1.40$, $\gamma_2 = 1.25$

$x_1 = 0.25$, $x_2 = 0.75$

$$\ln 1.40 = \frac{A^*}{\left[1 + \frac{A^* (0.25)}{B^* (0.75)}\right]^2} \quad \text{——— (1)}$$

$$\Rightarrow \ln 1.4 \left[1 + \frac{A^*}{3B^*}\right]^2 = A^* \quad \text{——— (3)}$$

$$\ln 1.25 = \frac{B^*}{\left[1 + \frac{B^* (0.75)}{A^* (0.25)}\right]^2} \quad \text{——— (2)}$$

$$\Rightarrow \ln 1.25 \left[1 + \frac{3B^*}{A^*}\right]^2 = B^*$$

$$\Rightarrow \ln 1.25 \left(\frac{3B^*}{A}\right)^2 \left[\frac{A^*}{3B^*} + 1\right]^2 = B^* \quad \text{——— (4)}$$

equation (4) ÷ eq^n (3)

$$\frac{\ln 1.25 \left(\frac{3B^*}{A^*}\right)^2 \left(\frac{A^*}{3B^*} + 1\right)^2}{\ln 1.4 \left(\frac{A^*}{3B^*} + 1\right)^2} = \frac{B^*}{A^*}$$

$$\frac{9}{1.5} \quad \frac{B^{*2}}{A^{*2}} = \frac{B^*}{A^*} \Rightarrow \boxed{\frac{B^*}{A^*} = \frac{1}{6}} \ \& \ \boxed{\frac{A^*}{B^*} = 6}$$

But in eq^n (3) & eq^n (4)

$$\ln 1.4 \left(1 + \frac{6}{3}\right)^2 = A^* \quad \Bigg| \quad \ln 1.25 \left(1 + \frac{3}{6}\right)^2 = B^*$$

$$\ln 1.4 (3)^2 = A^* \quad \Bigg| \quad \ln 1.25 (1.5)^2 = B^*$$

$$A^* = 3.02 \simeq 3 \quad \Bigg| \quad B^* = 0.5$$

Answer $(A^*, B^*) = (3.00, 0.5)$ option (ii)

Method - (II)

Van-Laar Activity coefficient A & B

given data: $\gamma_1 = 1.40$, $\gamma_2 = 1.25$

$x_1 = 0.25$ & $x_2 = 0.75$

$$A = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right]^2$$

$$A = \ln(1.4) \left[1 + \frac{0.75 \ln(1.25)}{0.25 \ln(1.4)} \right]^2$$

$$A = 3.0072 \simeq 3$$

$$\underline{A = 3}$$

$$B = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right]^2$$

$$B = \ln(1.25) \left[1 + \frac{0.25 \ln(1.4)}{0.75 \ln(1.25)} \right]^2$$

$$B = 0.5038 \simeq 0.5$$

$(A, B) = (3, 0.5)$ option (II) Answer.

VLE from k-value correlation ⇒

A convenient measure of the tendency of a given chemical species to partition itself preferentially b/w liquid and vapour phases is the equilibrium ratio K_i.

k-value

$$K_i = \frac{y_i}{x_i}$$

- It's tendency to favor the vapor phase.
  - If $K_i > 1$; species i exhibits a higher concentration in the vapour phase
  - If $K_i < 1$; Higher concentration in the liquid phase

* k-value :- The use of k-values allowing elimination of one set of mole fractions $\{y_i\}$ or $\{x_i\}$ in favor of the other.

1) k-value for Raoult's law :

$$y_i P = x_i P_i^{sat} \implies K_i = \frac{P_i^{sat}}{P}$$

2) k-value for Modified Raoult's law :-

$$y_i P = \gamma_i x_i P_i^{sat} \Rightarrow K_i = \frac{\gamma_i P_i^{sat}}{P}$$

* $K_i = \frac{y_i}{x_i} \Rightarrow y_i = K_i x_i$ if $\sum_i y_i = 1$ then

$$\sum K_i x_i = 1$$

* For bubble point calculation: where x_i are known

$$\sum_i K_i x_i = 1 \quad ; \quad \left(K_i = \frac{y_i}{x_i}\right)$$

* for dew point calculation; where y_i are known

$$\sum_i \frac{y_i}{K_i} = 1$$

* **Note** :- **Imp.**
1) for Raoult's law : (Ideal gas + Ideal liquid)

$$\text{K-value} = f(T, P) \text{ only}$$

2) for modified Raoult's law: (Ideal gas + Non-Ideal liquid)

γ = Activity coefficient = $f(T, x_i)$

$$\text{K-value} = f(T, P, x_i)$$

3) for Non-ideal gas and Non-ideal liquid :

[ϕ = fugacity coefficient = $f(T, y_i)$]

$$\text{K-value} = f(T, P, x_i, y_i)$$

Thermodynamic property Relations :-

1) $dU = TdS - pdV$; Internal energy (closed system)

2) $dH = TdS + Vdp$; Enthalpy

3) $dA = -pdV - SdT$; Helmholtz free energy

4) $dG = Vdp - SdT$; Gibbs free energy

Solution thermodynamics :-

fundametal property relation :-

The Gibbs free energy in any closed system

$G = f(T, P)$; $$d(nG) = (nV)\,dp - (nS)\,dT \quad \text{—— ①}$$

where n = is the total no. of moles of the system

→ Equation ① may be applied to a single-phase fluid in a closed system wherein no chemical reactions occur. ∴ for such a system the composition is necessarily constant

$$\therefore \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} = nV \quad \text{and} \quad \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -nS \quad \text{—— ②}$$

↳ at constant T ↳ at constant P

n = the numbers of moles of all chemical species are held constant.

* for a general case of a single-phase, open system that can interchange matter with its surroundings.

total Gibbs energy $nG = f(T, P)$

since material may be taken from or added to the system,

$$\boxed{nG = f(T, P, n_i)}$$

where n_i = the numbers of moles of the chemical species present (moles of species i)

The total differential of nG

$$\Rightarrow \quad d(nG) = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} dT + \sum_i \underbrace{\left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}}_{\text{Chemical potential}} dn_i \quad \text{--- (3)}$$

$\sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}$ = summation is over all species present

n_j indicates that all mole numbers except the ith are held constant

chemical potential : $$\boxed{\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j}} \quad \text{--- (4)}$$

↳ Driving force of mass transfer.

from eq^n (2), (3) & (4) (at const T, variable mass & composition)

Total Gibbs energy

$$\boxed{d(nG) = (nV)\,dP - (nS)\,dT + \sum_i \mu_i\, dn_i} \quad \text{--- (5)}$$

↳ fundamental property relation for single-phase fluid system.

FUGACITY :

It is widely used in solution thermodynamics to represent the behaviour of real gas. The name fugacity means fleetness or escaping tendency.

* **for pure gases** : (pure substances)

→ for an infinitesimal reversible change occuring in the system under isothermal conditions

$$dG = Vdp - SdT^{\,0}$$

$$\boxed{dG = V\,dp}$$

→ for 1 mole of an ideal gas $PV = RT \Rightarrow V = \frac{RT}{P}$

$$dG = \left(\frac{RT}{P}\right) dp$$

$$dG = RT\frac{dp}{P}$$

$$\int_{G_1}^{G_2} dG = RT\int_{P_1}^{P_2} d(\ln P)$$

$$\boxed{dG = RT\,d(\ln P)} \Rightarrow \boxed{\Delta G = RT\ln(P_2/P_1)} \quad \text{—— (1)}$$

↳ This equation is applicable only to Ideal gases

→ If, we represent the influence of pressure on Gibbs free energy of real gases by a similar relationship, then the true pressure in the above equation should be replaced by an 'effective pressure', which is known as "Fugacity".

$$P \longrightarrow f$$

$$\boxed{dG = RT\,d(\ln f)} \Rightarrow \boxed{\Delta G = RT\ln(f_2/f_1)} \quad \text{—— (2)}$$

↳ This eqn is applicable for Real or Ideal gases

$$\boxed{dG = RT\, d(\ln f)} \quad \text{--- (2)}$$

on integration, we get

$$\boxed{G = RT \ln f + C} \quad \text{--- (3)}$$

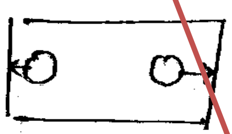
where C is a constant of integration

C = f (temperature and nature of gas)

* Fugacity :- It has the same dimension as pressure, usually Atmosphere or bar.

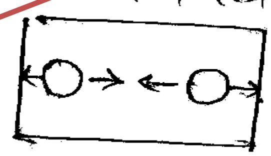
* Fugacity :

Ideal gas — No molecular intraction



$\frac{F}{A} = pr$

Real gas — molecular intraction exist



$\frac{f_{eff}}{A}$ = effective pr = fugacity (f)

If Attraction forces $f < pr$

If Repulsion forces b/w molecules $f > pr$

* In case of Ideal gas →

$$\Delta G = RT \ln (P_2/P_1)$$

$$\Delta G = RT \ln (f_2/f_1)$$

$$\Rightarrow \frac{f_2}{f_1} = \frac{P_2}{P_1} \Rightarrow \boxed{f \propto P} \text{ for ideal gases}$$

$$\frac{f}{P} = 1 \quad (\text{for convenience})$$

$$\boxed{f = P} \text{ for ideal gases}$$

→ The fugacity is always equal to the pressure for an ideal gas ($f = P$).

→ For Real gases, fugacity and pressure are not proportional to one another, and $\frac{f}{P}$ is not constant.

As the pressure of the gas is reduced, the behaviour of the real gas approaches that of an ideal gas.

So, at very low pressures, the fugacity of a real gas should be the same as its pressure

$\boxed{f = P}$ $\quad \lim_{P \to 0} \frac{f}{P} = 1$ or $\boxed{\frac{f}{P} \to 1 \text{ as } P \to 0}$ as low pressure

* **Fugacity coefficient →**

for same change in ΔG $\left\{ \begin{array}{l} \Delta G = RT \ln (P_2/P_1) \\ \Delta G = RT \ln (f_2/f_1) \end{array} \right\}$

$$\cancel{RT} \ln (P_2/P_1) = \cancel{RT} \ln (f_2/f_1)$$

$$\frac{P_2}{P_1} = \frac{f_2}{f_1}$$

$$f \propto P$$

$$\boxed{f = \phi P} \Rightarrow \boxed{\phi = \frac{f}{P}}$$

where, ϕ → fugacity coefficient

→ The ratio of fugacity to pressure is known as "fugacity coefficient". It is dimensionless and depends on nature of the gas, the pressure and the temperature.

PROPERTY CHANGE OF MIXING :-

Molar properties of an ideal solution is simply the average of the molar properties of the pure components, each weighted according to its mole fraction.

* for ideal solution $$M = \sum x_i m_i \quad \text{--- (1)}$$

* for Real solution $M \neq \sum x_i m_i$

 $(M = \sum x_i \overline{m}_i)$ $$M = \sum x_i m_i + \Delta M \quad \text{--- (2)}$$

Property change of mixing → $\Delta M = M - \sum x_i m_i$

$$\Delta M = \sum x_i \overline{m}_i - \sum x_i m_i$$

Imp:- $$\Delta M = \sum x_i (\overline{m}_i - m_i)$$

for ideal solution $M = \sum x_i m_i$

where M = Molar property of the solution

m_i = molar property of pure i

x_i = mole fraction of 'i'

for Real solution $M = \sum x_i m_i + \Delta M$

where ΔM = property change of mixing

1) Gibbs Energy change of mixing :→

the change in the free energy of a substance when it is brought from its standard state to the solution,

for component 'i' $dG_i = RT\,d\ln f_i$

$$G_i - G_i^{\circ} = RT\ln(f_i/f_i^{\circ}) \quad \text{——} \; (1)$$

for 'i' in solution

$$d\bar{G}_i = RT\,d\ln\hat{f}_i$$

$$\bar{G}_i - G_i^{\circ} = RT\ln(\hat{f}_i/f_i^{\circ}) \quad \text{——} \; (2)$$

eqn (2) - eqn (1)

$$\bar{G}_i - G_i = RT\ln(\hat{f}_i/f_i)$$

$$\boxed{\bar{G}_i - G_i = RT\ln a_i}$$

; a_i = Activity coefficent

$a_i = \hat{f}_i/f_i$

$$\Delta G = RT\ln a_i \quad \text{——} \; (3)$$

* the free energy change of mixing can be written as

$$\boxed{\Delta G = \Sigma x_i(\bar{G}_i - G_i)} \quad \Leftarrow \quad \Delta M = \Sigma x_i(\bar{M}_i - M_i)$$

—— (4)

from eqn (3) & (4)

$$\Delta G = \Sigma x_i(RT\ln a_i) \Rightarrow \frac{\Delta G}{RT} = \Sigma x_i \ln a_i$$

$$\Rightarrow \boxed{\frac{\Delta G}{RT} = \Sigma x_i \ln a_i} \quad \text{——} \; (*)$$

Imp.