

Binary (Solutions).

①

- ① A solution is defined as a homogenous mixture of ^{than one} or more substances having uniform properties throughout. Ex:
- ② Since it is a homogenous mixture, the solution constitute a single phase.
- ③ If the solution is two component (or Binary) system consisting of a solute and a solvent.
- ④ The solute is the component present in smaller proportion that dissolves to form the solution.
- ⑤ The solvent is the component present in bulk or larger proportions in which the solute dissolves.
- ⑥ The term solute and solvent do not signify any essential between the two components.
[Ethanol in water or water in ethanol]
- ⑦ A solution may exist in either of the states Solid or liquid or gas.
- ⑧ out of 9 type of soln significant type of soln
① Solid in liquid ② Liquid in liquid
③ Gas in liquid solutions.

We will primarily deal with liquid in liquid. ~~as per our syllabus.~~

Solutions of liquid in liquids;

- ① Binary liquid solutions, solutions consisting of two liquids.

- ② Both the liquids are supposed to be volatile.
 - ③ The solubility of a liquid in another liquid is determined by molecular structure of the solute and solvent.
 - ④ The general rule is like dissolves like.
 - ⑤ Similar Two substances having similar molecular structure & similar intermolecular forces of attraction are generally soluble in each other.
- Thermodynamics of Ideal solutions of liquids in liquids.

When a liquid is completely miscible with another liquid, a homogenous solution comprising of a single phase is formed.

If such a solution is placed in a closed evacuated vessel, the total pressure exerted by the vapour after the system has attained equilibrium will be equal to the partial pressures of the i -th constituents

A solution is said to be an ideal solution if its constituents follow Raoult's law under all conditions of composition.

Partial pressure of each and every constituent is given by $P_i = x_i P_i^*$

P_i = partial mol. fraction in pressure of the constituent i whose the solution is x_i & P_i^* is vapour pressure of the pure constituents.

The Thermodynamics of an Ideal solution:

The various constituents of an ideal solutions follow the relation.

$$\mu_i(\text{soln}) = \mu_i^* + RT \ln x_i$$

where $\mu_i(\text{soln})$ = chemical potential of the i th constituent of the solution. μ_i^* is the chemical potential of the pure liquid constituent x_i is the mol fraction of the constituent.

The changes in the thermodynamic functions when an ideal solution is formed by mixing pure components can be readily calculated.

$$\Delta G_{\text{mix}} = 0 \quad \Delta H_{\text{mix}} = 0 \quad \Delta V_{\text{mix}} = 0$$

$\Delta H_{\text{mix}} = 0$ implies at the molecular level the cohesive forces between the molecules of its constituents must be completely identical in nature.

For a binary molecule
A - A B - B & A - B the forces of attraction must be identical in the soln. Thus A molecule will not be able to know whether it is attracting B or A.

Also the molecules must have identical volumes so that $\Delta V = 0$.

- Examples
- (i) Ethylene Bromide & Propylene Bromide at 358K
 - (ii) Ethyl Bromide & Ethyl iodide at 303K.
 - (iii) n-Butyl Chloride & n-Butyl Bromide 323K.
 - (iv) n-Hexane & n-Heptane 303K.

Raoult's law: The partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution.

[F. Raoult studied number of binary solutions of volatile liquids at constant temperature & his generalization]

Since both the constituents of an ideal binary solution liquid system follow Raoult's law over the entire range of composition, the partial pressure exerted by the vapours of these constituents.

Let - a binary solution AB consisting of n_A moles of A & n_B moles of B (of two volatile liquids A & B)

Let - p_A = partial pressure of component A

p_B = partial pressure of component B.

$$p_A = x_A p_A^* \quad \& \quad p_B = x_B p_B^*$$

$$x_A = \frac{n_A}{n_A + n_B}, \quad x_B = \frac{n_B}{n_A + n_B}$$

are mol fraction of A & B.

p_A^* & p_B^* are vapour pressures of pure component A & B respectively.

Q If the vapours behaves ideally like gas

According to Dalton's law of partial pressure the total vapour pressure is

$$P = p_A + p_B = x_A p_A^* + x_B p_B^* \quad \text{--- (1)}$$

in sum Raoult's law $p_i = x_i p_i^*$ & total V.P = $P = \sum p_i$

A soln is called ideal if it obeys Raoult's law at all concn & temperatures.

$$P = x_A p_A^* + (1 - x_A) p_B^* \quad \left[\begin{array}{l} \because x_A + x_B = 1 \\ \text{or } x_A = 1 - x_B \\ \text{or } x_B = 1 - x_A \end{array} \right]$$
$$= p_B^* + (p_A^* - p_B^*) x_A \quad \text{--- (3)}$$

From the equation (3)

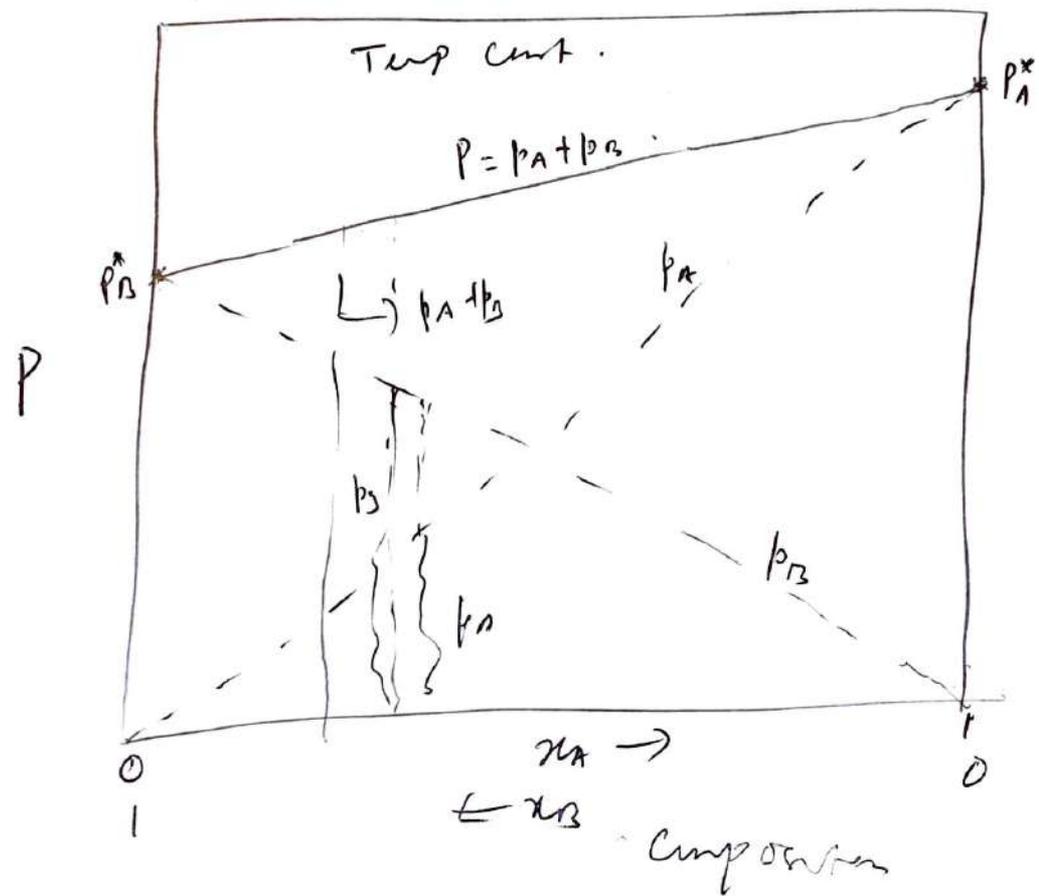
$$P = P_B^* + (P_A^* - P_B^*)x_A$$

It can be concluded the total vapour pressure of over the solution is a linear function of mole fraction of component A with intercept equal to P_B^* & slope equal to $(P_A^* - P_B^*)$

Hence the slope can be +ve or -ve depending upon the vapour pressure of pure component A & B, i.e. the magnitude of pure A & pure B.

If component A is more volatile than B $P_A^* > P_B^*$ $(P_A^* - P_B^*) = +ve$. In that total v.p. increases with increase in mole fraction of A.

If on the other hand component A is less volatile than B then $(P_A^* - P_B^*) = -ve$ as a result there will be decrease in total vapour pressure with increase in mole fraction of A i.e. of less volatile component.



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Total vapour pressure in terms of Mol fraction of the Component- A & B in terms of vapour.

The total vapour pressure P , can also be related to the mol fraction x_A & x_B of the two components in terms of vapour phase.

$$x_{A \text{ vap}} = y_A \quad \& \quad x_{B \text{ vap}} = y_B.$$

According to Dalton's law of partial pressure

$$y_A = \frac{p_A}{P} \quad \& \quad y_B = \frac{p_B}{P}.$$

$$p_A = x_A P_A^* \quad p_B = x_B P_B^*.$$

$$y_A = \frac{x_A P_A^*}{P} \quad \& \quad y_B = \frac{x_B P_B^*}{P}$$

$$\& \quad x_A P_A^* = y_A P \quad x_B P_B^* = y_B P.$$

$$P = p_A + p_B = x_A P_A^* + x_B P_B^*$$

$$P = P_B^* + (P_A^* - P_B^*) x_A$$

$$x_A = \frac{(P - P_B^*)}{(P_A^* - P_B^*)}$$

$$\boxed{\begin{aligned} x_A P_A^* &= y_A P \\ \frac{P_A^* (P - P_B^*)}{(P_A^* - P_B^*)} &= P y_A \end{aligned}}$$

$$\frac{P y_A}{P_A^*} = \frac{(P - P_B^*)}{(P_A^* - P_B^*)} \quad \text{---}$$

$$\& \quad P y_A (P_A^* - P_B^*) = P_A^* (P - P_B^*) \\ = P P_A^* - P_A^* P_B^*$$

$$P [y_A (P_A^* - P_B^*) - P_A^*] = -P_A^* P_B^*$$

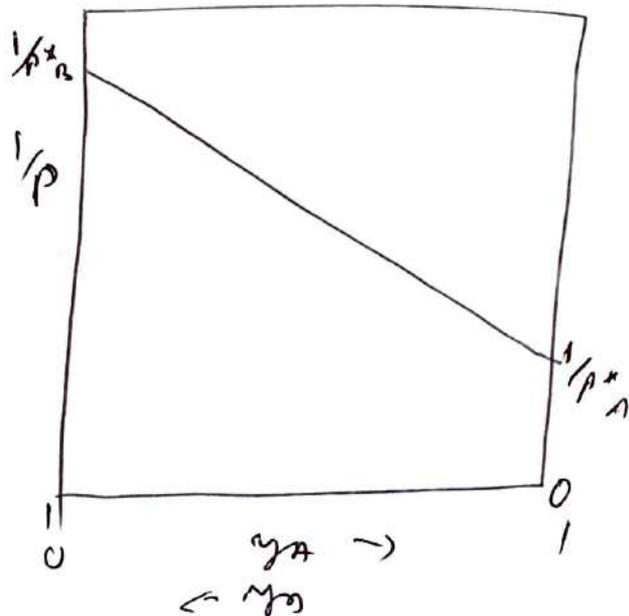
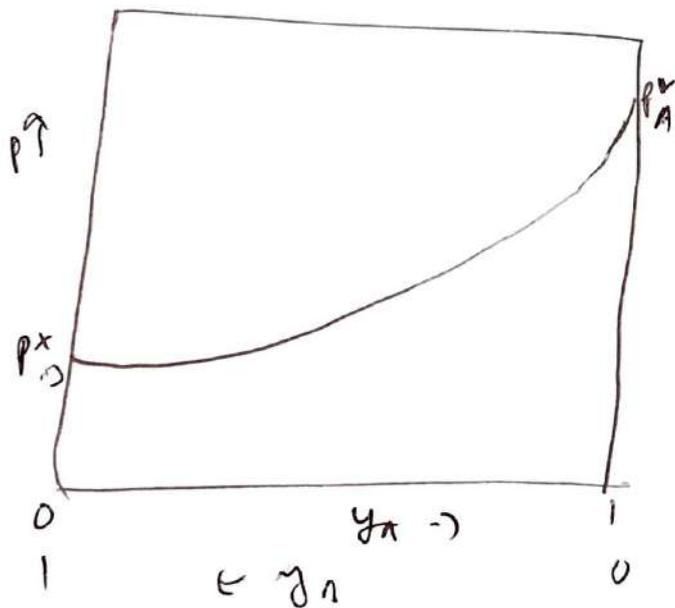
Multiply (-) to both A/B.

$$P = \frac{P_A^* P_D^*}{P_A^* + (P_D^* - P_A^*) y_A}$$

Plot of P vs y_A for a solution in which $P_A^* > P_D^*$

$$\frac{1}{P} = \frac{P_A^* + (P_D^* - P_A^*) y_A}{P_D^* P_A^*} = \frac{1}{P_D^*} + \left(\frac{1}{P_A^*} - \frac{1}{P_D^*} \right) y_A$$

The reciprocal of total pressure varies linearly with y_A , the mol fraction of component A in the vapour phase.



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Vapour pressure composition Diagram of a binary liquid solution:

Application of Phase Rule.

In a binary mixture no of components = 2.

According to phase rule $F = C - P + 2 = 4 - P$.

Variance of the system (Degrees of freedom) will depend on the number of phases present in a given system.

System comprising of a single phase (~~state~~), since a binary liquid mixture can be either in liquid phase or vapour phase.

$$P = 1 \Rightarrow F = 4 - P = 4 - 1 = 3.$$

Where pressure, composition & temperature has to be stated in order to define the system.

If one of them is held const i.e. temp system is studied under either const temp or const pressure or fixed composition, then $F = 2$, but only two values has to be specified as we have kept one value constant in that case we can represent the system in two dimensional (Rectangular Axis)

On the graphical representation of Raoult's Law.

P vs composition at ~~const~~ constant temperature.

$$(x_A + x_B = 1)$$

Imp on the curve plot of P vs composition at constant temperature (Total vapour pressure of a binary liquid mixture vs mol fraction ~~of~~ of component A ($x_A + x_B = 1$)) in the liquid phase.

Total pressure = Equilibrium vapour pressure.

System will comprise of only liquid phase if it is subjected to a pressure > Equilibrium vapour pressure. below it will be vapour phase.

System comprising of two phases:

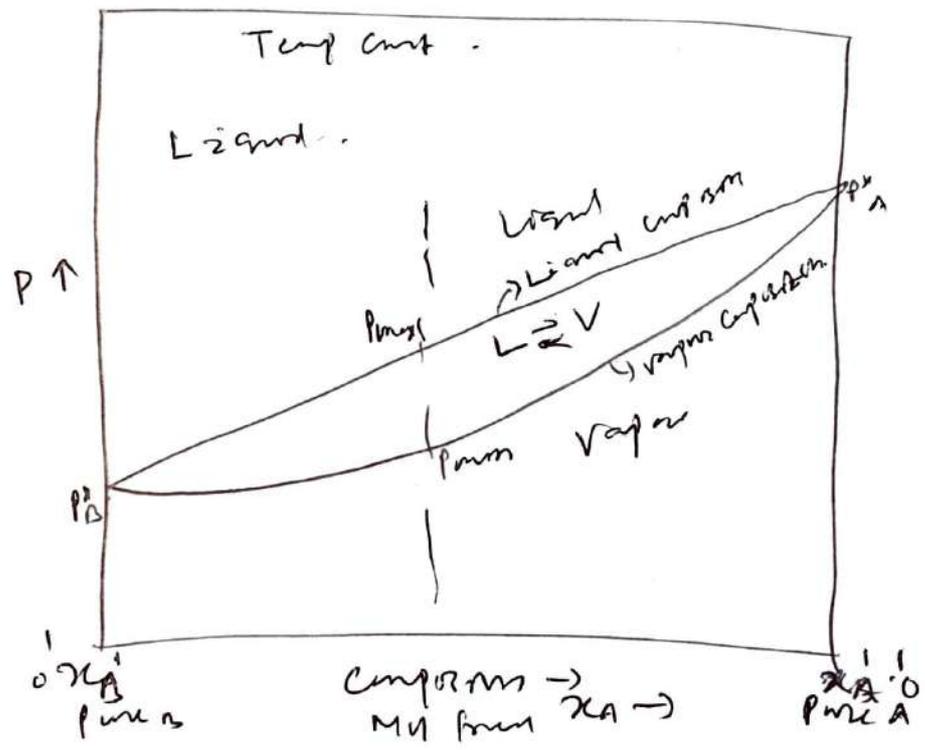
① If system exists in two phases i.e. in equilibrium with each other ($L \rightleftharpoons V$)

$$F = C - P + 2 = 2 - 2 + 2 = 2 \quad (F = 2)$$

② In order to define the system only two variables is sufficient to define the system. the third one will have a fixed value. (P, T, composition).

~~③ If temp & pressure stated~~

③ If we state Temperature & Composition than Pressure will have a fixed value.



④ As we have discussed the curve on Raoult's law. Deviation with liquid & vapor composition. The curves in the graph (drawn together).

⑤ Liquid curve & vapor curve.

Above liquid curve only liquid phase
Below vapor curve only vapor phase
& in between the two $L \rightleftharpoons V$. (Both liquid & vapor co-exist in equilibrium with each other.)

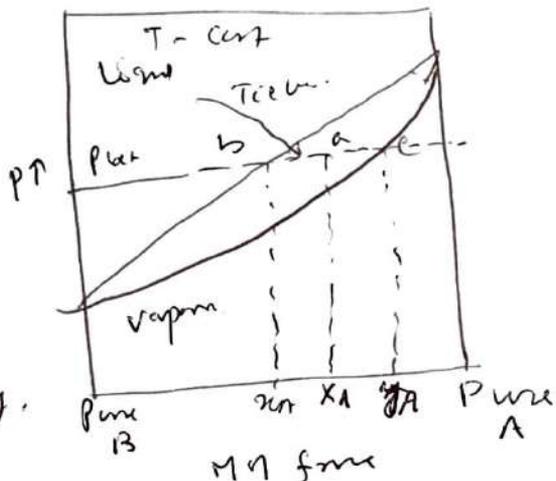
Along the line of the curves, both liquid & vapour co-exist.

We can summarize

- (i) $P_{system} > P_{max}$ only liquid phase.
- (ii) $P_{system} < P_{min}$ only vapour exist.
- (iii) $P_{max} > P_{system} > P_{min}$ (L \rightleftharpoons V) liquid & vapour phase in equilibrium with each other

Lever Rule:

①  → The region in the curve where both (L \rightleftharpoons V) liquid & vapour co-exist in equilibrium with each other.



② For this region $P=2$ & $F=2$
Since temperature is fixed then any of the 2 variable is sufficient to define the system (P, x_A & y_A) completely.

③ If P is chosen then the amount of liquid & vapour are represented by the intersection point of the horizontal line is known as the tie line drawn from the given P with those of liquid & vapour curves.

④ If x_A is chosen as the described variable, then the intersection of a vertical line from x_A with the liquid curve yields the value of P and a horizontal line from P cutting the vapour curve gives the vapour composition y_A .

⑤ A point within the liquid and vapour curves represents two phases, liquid & vapour in equilibrium with each other

⑥ The mole fraction of liquid component is reported by x_A & vapour phase y_A (point b & c)

Quantitative Introduction of the Lever Rule:

① Any point on the tie line represents the same composition of liquid & vapour phase namely x_A & y_A . The only difference that exists from point to point is relative amount of liquid & vapour phase.

② If it coincides with b vapour phase has begun & if it coincides with a mol fraction y_A & if it coincides with c then the liquid drop with x_A is just going to be converted to vapour keeping the mol fraction of the two phases x_A & y_A respectively.

③ If the point is nearer to b large amount of liquid & nearer to c large amount of vapour.

b_a — Amount of vapour formed
 c_a — Amount of liquid formed.

Distance ab is Amount of vapour formed
 Distance ac is Amount of liquid formed

$$\frac{ab}{ac} = \frac{\text{Amount of vapour formed}}{\text{Amount of liquid formed}} \quad (\text{Lever Rule})$$

Quantitative Derivation of Lever Rule:

x_A = Mol fraction composition of liquid & vapour phase

$$x_A = \frac{n_A(l) + n_A(v)}{n_A(l) + n_B(l) + n_B(v)} \quad \text{--- (1)}$$

$$ab = x_A - x_A = x_A - \frac{n_A(l)}{n_A(l) + n_B(l)} \quad \text{--- (2)}$$

$$ac = y_A - x_A = \frac{n_A(v)}{n_A(v) + n_B(v)} - x_A$$

Multiplying (1) $n_A + n_B(l)$ and eqn (2) by

$$n_A(v) + n_B(v) \quad \text{--- (3)}$$

$$n_A(l) + n_B(l) (ab) = n_A(l) + n_B(l) - x_A - n_A(l) \quad \text{--- (4)}$$

$$n_A(v) + n_B(v) (ac) = n_A(v) - (n_A(v) + n_B(v)) x_A$$

Subtracting eqn (4) - (3)
 and putting the value of $X_A = \frac{n_{A(l)} + n_{B(l)}}{n_{A(l)} + n_{B(l)} + n_{A(v)} + n_{B(v)}}$

$$n_{A(l)} + n_{B(l)} (a_b) - n_{A(v)} + n_{B(v)} a_c = X_A (n_{A(l)} + n_{B(l)} + n_{A(v)} + n_{B(v)}) - n_{A(v)} + n_{B(v)} \quad \text{--- (5)}$$

Substituting the value of X_A in eqn (5)

$$n_{A(l)} + n_{B(l)} (a_b) - n_{A(v)} + n_{B(v)} (a_c) = 0$$

$$\frac{a_b}{a_c} = \frac{n_{A(v)} + n_{B(v)}}{n_{A(l)} + n_{B(l)}}$$

$$\frac{a_b}{a_c} = \frac{\text{Amount of vapour phase}}{\text{Amount of liquid phase}}$$

Ratio of amount of vapour to the amount of liquid is given by the ratio lengths of the line segments connecting a to b & a to c. Thus if a lies very close to b a_b is very small hence $n_v \ll n_l$. * System comprises mainly of liquid phase on the other hand if a lies very close to c then $n_v \gg n_l$. the system consists mainly of vapour phase.