Solutions

Active mass refers to the amount of substances which is active or available in the reaction and can be taken as the molecular Concentration of the Substance present.

Solutions: is a homogeneous mixture of two or more substances it is a single phase, whether it be gaseous, liquid or solid.

رأولت

Ideal Solutions ; Raoult's Law

Raoult's Law: States that the relative lowering of the vapour pressure of a solvent (مذيب) due to the addition of a solute (مذاب) is equal to the molecular fraction of the solute in the solution.

Ex A and B two substances forming a solution, each substance exerts its own vapour pressure P_A and P_B respectively at any particular Composition of the Solution, and the total vapour pressure (P) of the Solution is equal to $P_A + P_B$. Let P_A° and P_B° be the vapour pressure exerted by the pure substances, A and B respectively then, according to Raoult's law, if X_A and X_B are the mole fractions of A and B respectively $\Rightarrow$

$$\frac{P_A^\circ - P_A}{P_A^\circ} = X_B \quad \text{and} \quad \frac{P_B^\circ - P_B}{P_B^\circ} = X_A$$

$$\left[\begin{array}{l} X_A = \frac{P_A}{P_A^\circ} \\ X_B = \frac{P_B}{P_B^\circ} \end{array} \right\} \quad X_C = \frac{P_C}{P_C^\circ}$$

$$1 = X_A + X_B + X_C$$

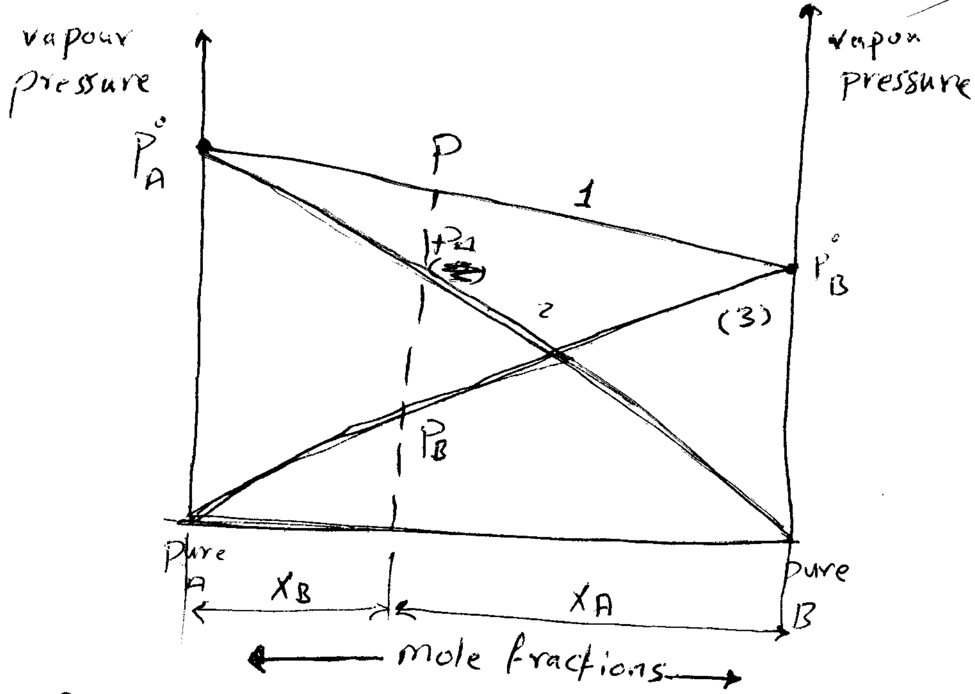
$$1 - \frac{P_A}{P_A^\circ} = X_B$$

$$\frac{P_A}{P_A^\circ} = 1 - X_B$$

but $X_A + X_B = 1$ and therefore $\frac{P_A}{P_A^\circ} = X_A$

and similarly $\frac{P_B}{P_B^\circ} = X_B$

This means that if a solution obeys Raoult's law the vapour pressure of one of the Components of that solution is directly proportional to the mole fraction of that Component in the solution. The Constant of proportionality is the vapour pressure of the Component in its pure state



Representation of Raoult's law for a binary solution of A and B

The straight line (1) shows the variation of the vapour pressure of the solution with variation in the composition of the solution. The effect of change in composition of the solution on the pressures exerted by A and B separately is shown by the straight lines (2) and (3) respectively.

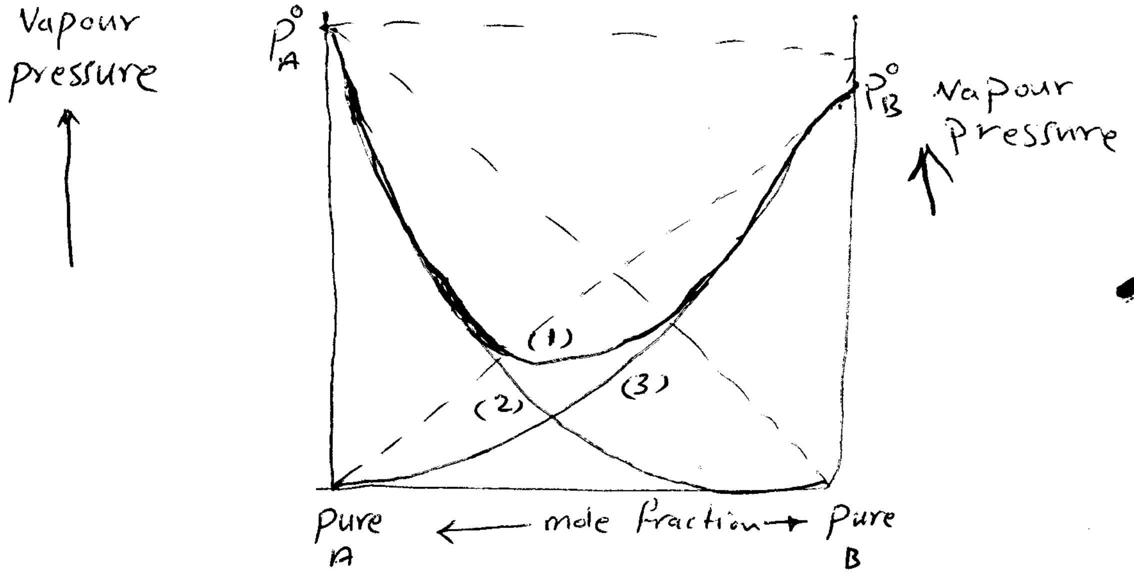
(*) A solution which obeys Raoult's law is called an "ideal solution". The molecules of A and B must be of similar size and must attract one another with the same force as the molecules of A attract other molecules of A, or molecules of B attract other molecules of B and also the vapour should behave as as an ideal gas for the solution to obey Raoult's law.

② ((Deviations from Raoult's Law))

① Attraction between molecules of A or B.

negative deviation from Raoult's law.

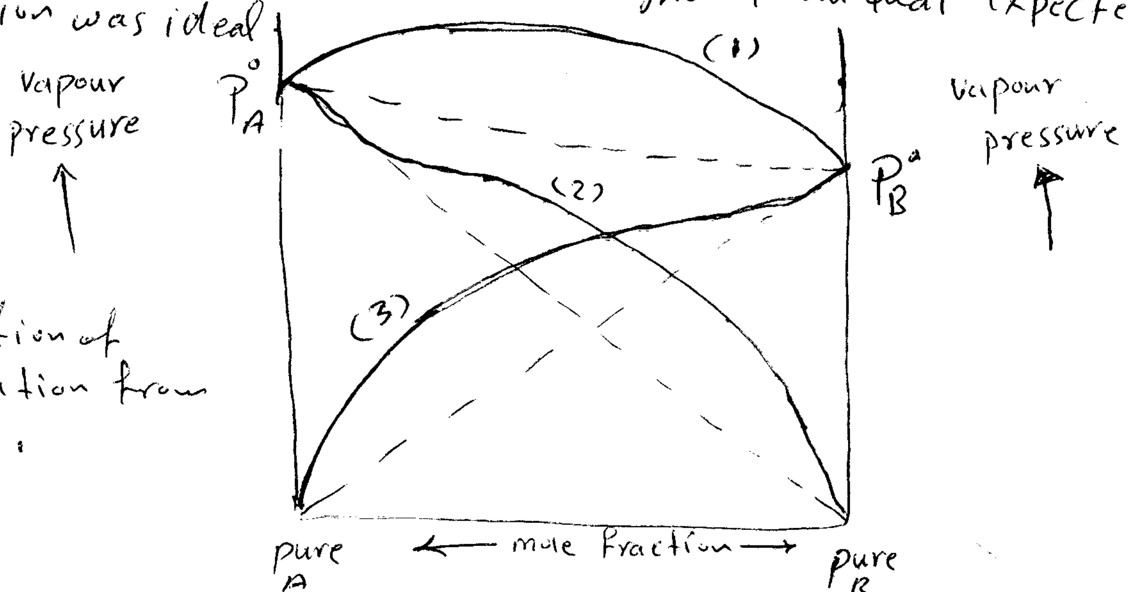
if A attracts B more strongly than the mutual attraction of A (A-A) or B (B-B) molecules. The vapour pressure exerted by each component of the solution will be lower than that expected if the solution was ideal. (A-B) > (A-A) or (B-B)



Representation of negative deviation from Raoult's law for binary solution of A and B. (1) represents the vapour pressure of the solution, and solid curve (2) and (3) represent the vapoure pressure by A (P_A) and B (P_B) respectively. Dotted line indicate the conditions for an ideal solution.

⊛ positive deviation from Raoult's law.

if the attraction between A and B molecules is weaker than the mutual attraction of Ⓐ molecules or B molecules. The vapour pressure exerted by each component of the solution will be higher than that expected if the solution was ideal



Representation of positive Deviation from Raoult's Law.

② A difference in size between the Components of a solution (A and B) will affect the distance between the Centres of adjacent particles and Consequently the attraction between them.

③ if a gas dose not behave ideally, we can define a quantity fugacity Φ so that, under all Conditions

قررين؟

$$\Phi V = RT$$

In metallurgical processes, we are normally Concerned with gas at low pressure or high temperature - where effects of intermolecular attraction and the volume occupied by the molecules is insignificant - so that we can assume that the pressure exerted by gases are equal to their fugacities - that is they are ideal and obey the Ideal Gas equation

$$\boxed{PV = RT}$$

(*) **Activities** :- in actual solution the vapour pressure of a Component is not directly proportional to the mole fraction of that Component and Can either be greater or less than that expected from the Solution if it obeyed Raoult's law.

we can define the (activity) a_A of the Substance A in the Solution

$P_A = P_A^\circ \cdot a_A$; $P_B = P_B^\circ \cdot a_B$, a_A and a_B the activity of A substance and B s.

for an ideal solution, $P_A = P_A^\circ \cdot X_A$; $P_B = P_B^\circ \cdot X_B$ $\Rightarrow \boxed{a_A = X_A}$

But if the Solution deviates from Raoult's law $\Rightarrow \boxed{a_A = \gamma_A \cdot X_A}$

معامل النشاط

wher γ_A is Raoultian activity Coefficient

$\gamma = \dfrac{a}{X}$ — γ greater than unity for a positive deviation; γ less than Unity for a negative deviation

for a pure Substance A $\gamma_A = 1$ and $X_A = 1$, so that we have Unit activity of Substance A which is in its "standard state"

* where the activity of a substance is changed from a_1 to a_2 the free energy change involved is $\boxed{\Delta G = RT \ln \frac{a_2}{a_1}}$

It should be noted that the activity Coefficient of a substance in Solution can vary with the Concentration of that substance in the solution.

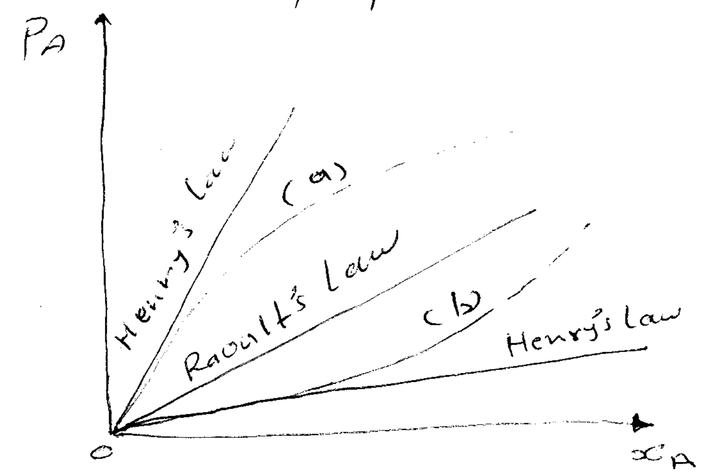
Henry's Law and Dilute solutions:-

Henry's Law :- States that the mass of a gas dissolved by a given Volume of solvent, at Constant temperature is proportional to the pressure of the gas in equilibrium with the solution. This law is more general than Raoult's law, which states that the Constant of proportionality is the vapour pressure of the pure substance.

Henry's law = $P_A \propto X_A$

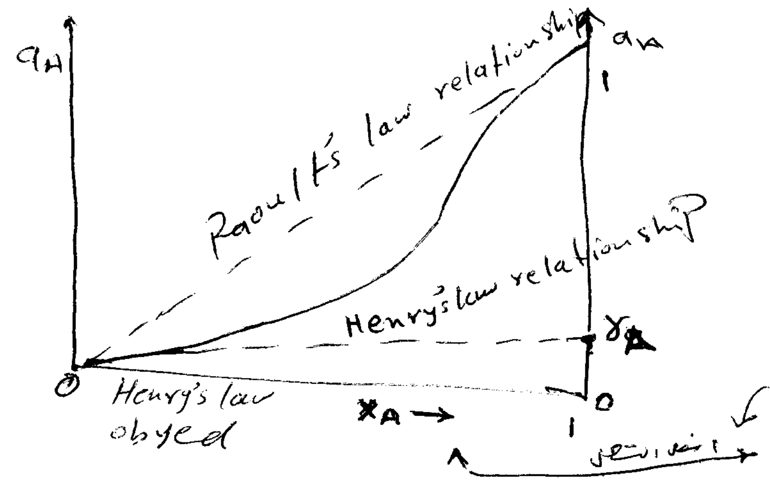
Raoult's Law = $P_A = P_A^o \cdot X_A$

In very dilute solution, Henry's law is obeyed by the Solute, and that the vapour pressure of the solute is proportional to it's Concentration.



Graph of vapour pressure of solute against mole fraction at Low Concentration of Solute for (a) a positive deviation from Raoult's law and (b) a negative deviation from Raoult's law. Both Curves (a) and (b) approximate to a straight line at low Concentration and are the obeying Henry's Law

(*) This figure shows the relationship between the activity of solute and the Concentration when a solute obeys Henry's Law.



Graph of Raoultian activity of Solute A against mole fraction of A showing Value of γ_A^o, the Raoultian activity Coefficient of A at infinite dilution.

Ex:. The activities of Aluminum at different Concentration in Aluminum - Copper Solution at 1100°C is given below

X_{Cu}	0.1	0.25	0.37	0.47	0.55	0.62	0.7	0.9
a_{Al}	0.89	0.69	0.5	0.53	0.2	0.1	0.03	0.0008

Calculate the activity Coefficient of Aluminum in Solution Contains 20% Aluminum. [illegible]

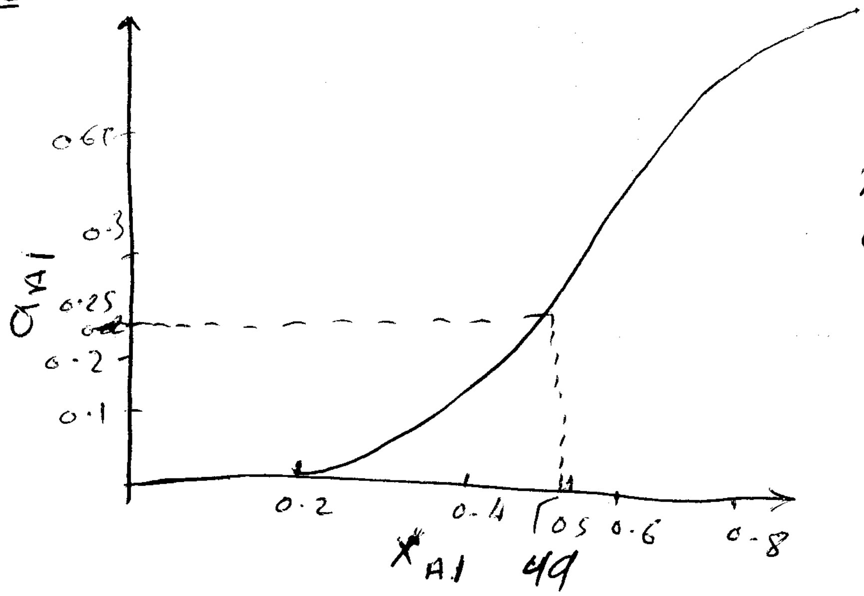
X_{Cu} 0.1 – 0.25 – 0.37
X_{Al} 0.9 – 0.75 – 0.63

Ex:. The activities of Aluminum at different Concentrations in Al-Cu Solution at 1100 given by

X_{Al}	0.1	0.2	0.3	0.38	0.45	0.53	0.63	0.75	0.9
a_{Al}	0.008	0.005	0.003	0.1	0.2	0.32	0.5	0.69	0.89

Calculate the activity Coefficient of Aluminum at Concentration of 49% Al.

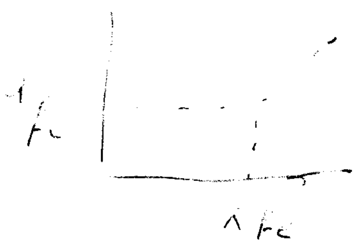
Ans



$X_{Al} = 0.49$

$a_{Al} = 0.25$

$$\gamma_{Al} = \frac{a_{Al}}{X_{Al}} = \frac{0.25}{0.49} = 0.5102$$



$\bar{a}_{Fe} = X_F \cdot \gamma_{Fe}$