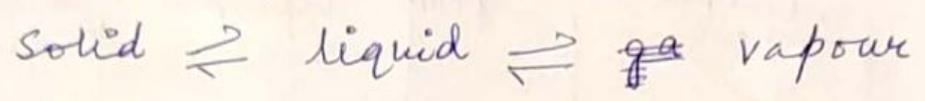


★ Phase Diagram of water System :

Water system is a one component system. In water, there are 3 phases - solid, liquid and vapour. The 3 single phases may occur in equilibrium -

- i) liquid \rightleftharpoons vapour
- ii) Solid \rightleftharpoons vapour
- iii) Solid \rightleftharpoons liquid.

The 1 three phase eq^lm is -



From the phase rule equation, $F = c - P + 2$, when all the 3 phases are present together, the degrees of freedom,

$F = c - P + 2 = 1 - 3 + 2 = 0.$

Thus, the system is invariant or non-variant. when only two phases exist at the time of eq^lm, the degrees of freedom,

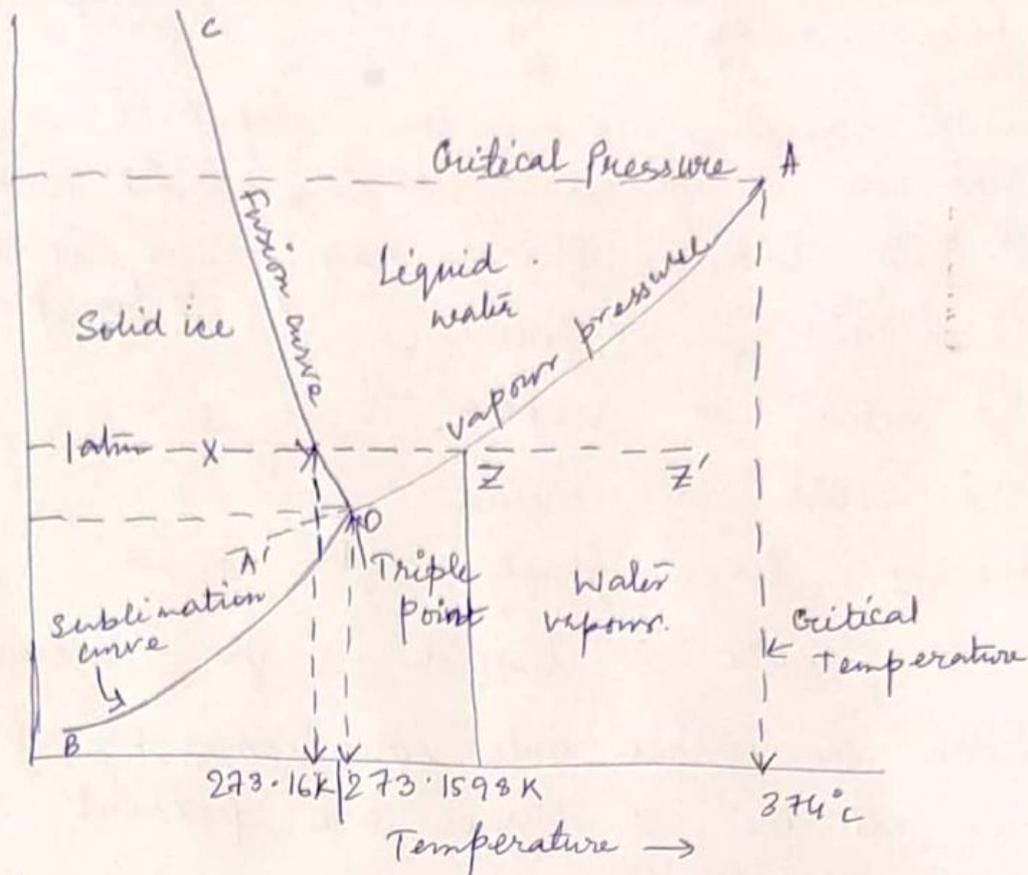
$F = c - P + 2 = 1 - 2 + 2 = 1.$

i.e., the system is univariant or monovariant.

If only a single phase is present, then

$F = c - P + 2 = 1 - 1 + 2 = 2.$

i.e., each single phase at equilibrium possesses 2 degrees of freedom or the system is bivariant. It means that both temperature and pressure can be varied without disturbing the eq^lm.



Curve OA:

It represents the eqbm between liquid water and vapour at different temperatures. At any given temperature, there is one and one pressure at which water vapour is in eqbm with liquid water. The degree of freedom is one. From phase rule:

$$F = C - P + 2 = 1 - 2 + 2 = 1.$$

Curve OB:

It represents the eqbm between ice and vapour at different temperatures. It is called the sublimation curve of ice or the vapour pressure curve of ice. The degree of freedom is one or the system is univariant in accordance with the phase rule. The slope of the curve is (+) ve.

Curve OC: This curve represents the eqbm between ice and liquid water. It is called the fusion curve of ice. The slope of this curve is (-) ve.

The point 'O': The 3 curves, OA, OB, and OC meet at point 'O' at which solid, liquid and vapour phase coexist in eqbm. It is known as triple point. Since, three phases coexist, the system is invariant. The number of degrees of freedom is zero.

Duhem - Margules Equation:

According to Gibbs' - Duhem equation for binary system of two components A and B,

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \dots (i)$$

where n_A and n_B are the number of moles of components A and B respectively in the solution and μ_A and μ_B are their chemical potentials.

Dividing equation (i) by $(n_A + n_B)$,

$$\frac{n_A}{n_A + n_B} d\mu_A + \frac{n_B}{n_A + n_B} d\mu_B = 0.$$

$$\text{or, } x_A d\mu_A + x_B d\mu_B = 0 \quad \dots (ii)$$

where x_A , x_B represents the mole fractions of components A and B in the solution.

The chemical potential of any component in the solution depends upon temperature, pressure, composition of the solution. Hence, if the temperature and pressure are kept constant, the chemical potential depends only upon the composition.

For an infinitesimal change of composition,

$$d\mu_A = \left(\frac{\partial \mu_A}{\partial x_A} \right)_{T,P} dx_A \quad \dots (iii)$$

$$d\mu_B = \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T,P} dx_B \quad \dots (iv)$$

Substituting these values in eqn. (ii),

$$x_A \left(\frac{\partial \mu_A}{\partial x_A} \right)_{T,P} dx_A + x_B \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T,P} dx_B = 0 \quad \text{--- (v)}$$

Now, $x_A + x_B = 1$

$$\therefore dx_A + dx_B = 0.$$

$$dx_A = -dx_B$$

Substituting these values in eqn. (v), we get,

$$x_A \left(\frac{\partial \mu_A}{\partial x_A} \right)_{T,P} dx_A - x_B \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T,P} dx_A = 0.$$

$$\text{or, } x_A \left(\frac{\partial \mu_A}{\partial x_A} \right)_{T,P} - x_B \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T,P} = 0.$$

$$\text{or, } x_A \left(\frac{\partial \mu_A}{\partial x_A} \right)_{T,P} = x_B \left(\frac{\partial \mu_B}{\partial x_B} \right)_{T,P} \quad \text{--- (va)}$$

$$\text{or, } \left(\frac{\partial \mu_A}{\partial \ln x_A} \right)_{T,P} = \left(\frac{\partial \mu_B}{\partial \ln x_B} \right)_{T,P} \quad \text{--- (vi)}$$

This is another form of Gibb's Duhem eqn.

The chemical potential μ_i of any component i of a liquid mixture given by -

$$\mu_i(\text{sol}) = \mu_i^\circ + RT \ln p \quad \text{--- (vii)}$$

where p is the partial vapour pressure and μ° is the std chemical potential of that component. The above relation was derived by assuming that the vapour behaves as an ideal gas. For components A & B,

$$\mu_A = \mu_A^\circ + RT \ln p_A \quad \text{--- (viii)}$$

$$\mu_B = \mu_B^\circ + RT \ln p_B \quad \text{--- (ix)}$$

Differentiating eqn. (viii) w.r. to x_A and eqn. (ix) w.r. to x_B , at constant temperature, we get,

$$\frac{d\mu_A}{dx_A} = RT \frac{d \ln p_A}{dx_A} \quad \text{--- (ix)}$$

$$\frac{d\mu_B}{dx_B} = RT \frac{d \ln p_B}{dx_B} \quad \text{--- (x)}$$

Multiplying eqn (i) & (ii) by x_A and x_B resp. ly, we get,

$$x_A \frac{d \mu_A}{d x_A} = x_A \cdot RT \frac{d \ln p_A}{d x_A} \dots (xi)$$

and $x_B \frac{d \mu_B}{d x_B} = x_B \cdot RT \frac{d \ln p_B}{d x_B} \dots (xii)$

From (xi) & (xii), (va), we get,

$$x_A \cdot RT \frac{d \ln p_A}{d x_A} = x_B \cdot RT \frac{d \ln p_B}{d x_B}$$

or, $x_A \cdot \frac{d \ln p_A}{d x_A} = x_B \frac{d \ln p_B}{d x_B}$

or, $\boxed{\frac{d \ln p_A}{d \ln x_A} = \frac{d \ln p_B}{d \ln x_B}} \dots (xiii)$

This eqn is known as Schem-Margules eqn and relates the partial pressures of the two components with their corresponding mole fractions. It is applicable to both ideal and non-ideal liquid mixtures.

Eqn (xiii) can also be written as -

$$\boxed{\left(\frac{\partial \ln p_A}{\partial \ln x_A} \right)_{T,P} = \left(\frac{\partial \ln p_B}{\partial \ln x_B} \right)_{T,P}} \dots (xiv)$$

Konowaloff's Rule:

Let us consider the total vapour pressure, P_i in terms of mole fractions of the components in the vapour phase. The mole fraction of A in vapour phase is γ_A and that of B is γ_B .

If p_A and p_B are the partial vapour pressures of the components A and B in the vapour phase, then according to Dalton's law of partial pressures

$$\begin{aligned}
 Y_A &= \frac{p_A}{P} = \frac{p_A^\circ \cdot x_A}{p_A^\circ \cdot x_A + p_B^\circ \cdot x_B} \\
 &= \frac{p_A^\circ (1-x_B)}{p_A^\circ (1-x_B) + p_B^\circ x_B} = \frac{(1-x_B) p_A^\circ}{(p_B^\circ - p_A^\circ) x_B + p_A^\circ} \quad \dots \dots (i) \\
 Y_B &= \frac{p_B}{P} = \frac{p_B^\circ x_B}{p_A^\circ x_A + p_B^\circ x_B} \\
 &= \frac{p_B^\circ x_B}{(p_B^\circ - p_A^\circ) x_B + p_A^\circ} \quad \dots \dots (ii)
 \end{aligned}$$

Dividing eqn. (ii) by (i), we get,

$$\frac{Y_B}{Y_A} = \frac{p_B^\circ \cdot x_B}{p_A^\circ \cdot x_A} = \frac{x_B}{x_A} \cdot \frac{p_B^\circ}{p_A^\circ} \quad \dots \dots (iii)$$

Thus, if B is more volatile than A, i.e.,

$$\text{if } p_B^\circ > p_A^\circ \text{ or, } \frac{p_B^\circ}{p_A^\circ} > 1$$

$$\text{then } \frac{Y_B}{Y_A} > \frac{x_B}{x_A}$$

This ~~and~~ means that the vapour phase is richer in the more volatile component B than the liquid phase from which it vapourises. The mole fraction of the more-volatile component is always greater ~~than~~ in the vapour phase than in the solution phase, i.e., ratio $\frac{Y_B}{Y_A}$ is greater than one. This result is known as Konovaloff's rule.

This rule predicts the composition of the vapour phase for mixtures of volatile liquids of different compositions at constant temperature.

Henry's law :

Mass of a gas dissolved per unit volume of a solvent is directly proportional to the pressure of the gas in equilibrium with the solution at a given temperature.

Mathematically, $m \propto p$

where 'm' is the mass of the gas dissolved per unit volume of a solvent and 'p' is the pressure of the gas in equilibrium with solution.

$$m = Kp.$$

$$\text{or, } \left[\frac{m}{p} = K \right] = \text{constant}$$

K is called Henry's law constant, is characteristic of the nature of the gas, the nature of the solvent and the temperature of the gas.

Limitations of law :

Henry's law is valid only if :-

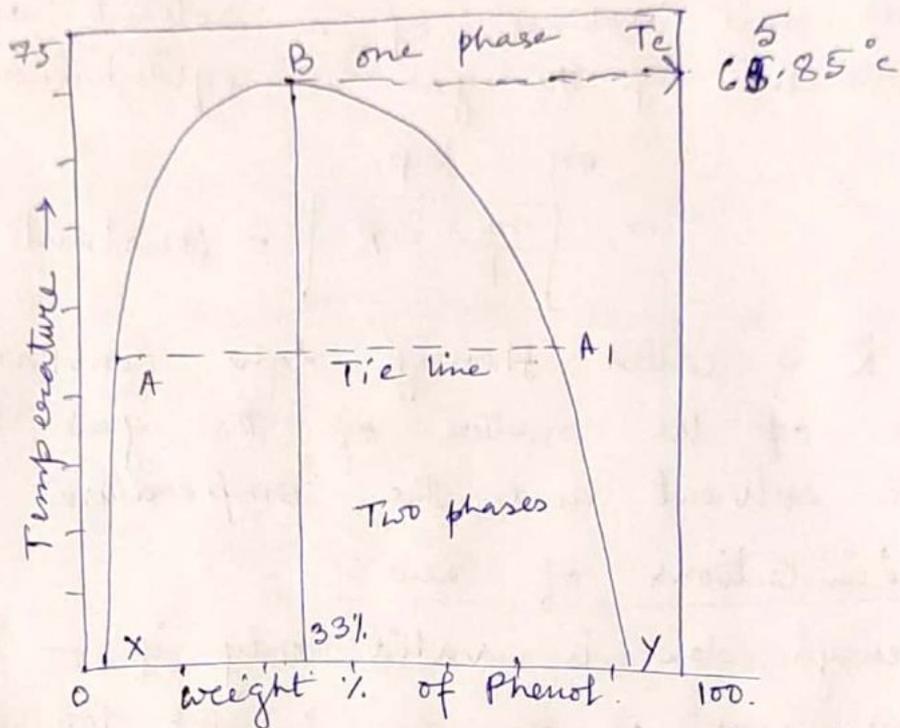
- (i) pressure of the gas is not too high.
- (ii) the gas is only sparingly soluble.
- (iii) Gas does not enter into chemical combination with the solvent
- (iv) Gas does not dissociate or associate in the solvent.

Azeotropes :

Mixtures of liquid which boil at constant temperature like a pure liquid such that the distillate has the same composition as that of liquid mixture are called constant boiling mixtures or azeotropic mixtures or azeotropes.

- i) Minimum boiling azeotropes: Eg → water and ethyl alcohol. (show (+)ve deviation)
- ii) Maximum boiling azeotropes: (→) ve deviations from ideal behaviour. Eg → mixture of H₂O and HCl.

Phenol - Water Binary System Upper critical Solution Temperature Type:



When phenol is added to water, two layers are produced. ~~one~~ The lower layer will consist of a solution of phenol in water and the upper layer will consist of a solution of water in phenol.

In the figure, the curve YB represents the solubility curve of water in phenol and XB represents the solubility of phenol in water.

The following observations are made -

- i) On increasing temperatures, the mutual solubility of two liquids increases.
- ii) At ~ 66°C, the two curves join smoothly at B.

i.e., the composition of two layers becomes identical and two liquids become completely miscible. In other words, at $\approx 66^\circ\text{C}$ and above, phenol and water are completely miscible in all proportions and yield only a single layer on mixing.

At a temperature lower than 66°C , 'A' represents the composition of water rich layer and 'A'' represents the composition of phenol rich layer, in eq^m with A.

All compositions between pure water and 'A' yield a solution of water in phenol.

The domed-shaped area represents the two phases in eq^m while outside the domed-shaped area, we have only one phase. The temperature corresponding to point 'B' represents the temperature above which the 2 liquids are completely miscible in all proportions. It is critical solution temperature (CST). Since CST ~~is~~ corresponds to the maximum point of the curve, it is termed upper critical solution temperature (UCST).