Phase Equilibria

Definitions :-

1. Phase → A phase is defined as any homogeneous and physically distinct part of a system, separated from other parts of the system by well defined bounding surface and is mechanically separable from other parts of the system.

If in a system water, ice, liquid water and water vapour co-exist, each form constitutes a different phase and each phase is separated from each other by a phase boundary. This boundary is known as interface.

Since all gases are completely miscible in all proportions, they form only one phase. A system consisting of one phase only is said to be homogeneous.

Solids generally constitute separate phases except when they form a solid solution. In the decomposition of calcium carbonate into calcium oxide and carbon dioxide there are two solid phases and one gas phase present at equilibrium. It is, therefore, a three phase system

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Systems having more than one phase are called heterogeneous systems.

2. Components → The number of components in a system at equilibrium is defined as the minimum number of independently variable consituents in terms of which the composition of each phase can be expressed by means of a chemical equation. The concept of components will become clear if we consider the following examples:

In the system "water," the phases that are present are ice, liquid water and water vapours. The composition of each of the three phases can be expressed in terms of the single component water and thus, water system is only a one component system.

3. Degree of Freedom → The degree of freedom or variance of a system is defined as the smallest number of independent variables, such as, pressure, temperature and concentration which can be altered without varying the total number of phases present in the system.

Considering a system consisting of a gas enclosed in a cylinder provided with a movable piston. It is a single phase system. To describe completely the state of such system, we need only temperature and pressure as the volume is automatically known from the equation of state. The system is thus said to be bivariant. In other words, it was two degrees of freedom or the variance,

$$F = 2.$$

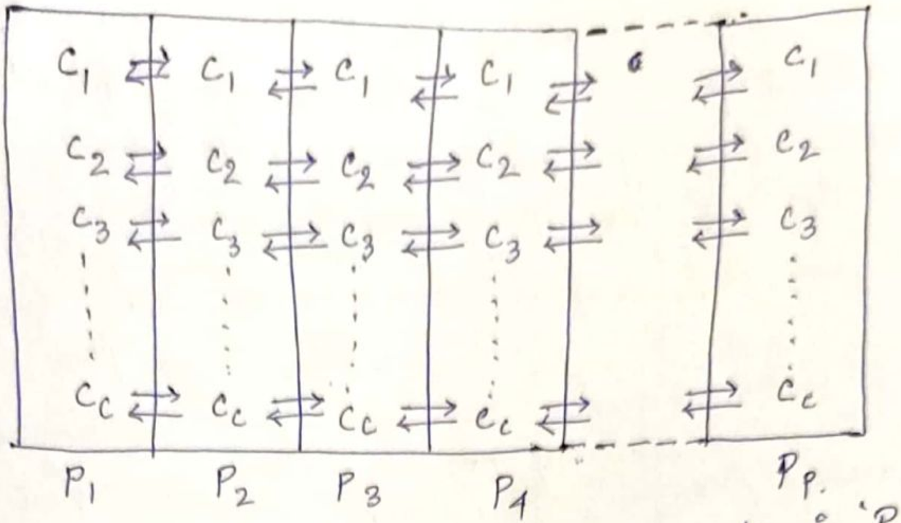
★ PHASE RULE:

The phase rule states that, if the equilibrium in a heterogeneous system is not influenced by electrical, magnetic or gravitational forces, the number of degrees of freedom (F) of the ~~freedom~~ system, the number of components (C) and the number of phases (P) of the system are related by the equation:

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

Deduction of Phase Rule:

Consider a heterogeneous system in equilibrium consisting of 'C' components ($C_1, C_2, C_3 ---- C_c$)



Distribution of 'c' components in 'p' phases.

The system at equilibrium can be completely described if the values of the variables ~~listed~~ are known —

Variable	Number
i) Temperature	1
ii) Pressure of the system	1
iii) conc^n of each and every component in all the 'p' phases. For each phase, values of 'c' conc^n terms are to be specified. Hence, for 'p' phases, 'pc' conc^n terms are to be specified.	pc
Total no. of variables to be specified.	= pc + 2

In each phase, there is a relationship between the mole fractions.

$$x_1 + x_2 + x_3 + \cdots + x_c = 1 \quad \text{----} \ (i)$$

using eq^n (i), we can calculate the mole fraction of any component in a phase if the mole fractions of all other components are known. For each phase there is one such eq^n and for 'p' phases, there are 'p' eq^n similar to eq^n (i). Therefore, the total number of independent variables to be specified are —

$$cp + 2 - p \quad \text{. or,} \quad p(c-1) + 2$$

When a heterogeneous system is in eqlm at constant temperature and pressure, the chemical potential of any component will have the same value in all the 'p' phases, i.e.,

$$\mu_1^{(1)} = \mu_1^{(2)} = \mu_1^{(3)} = \cdots = \mu_1^{(P)}$$

$$(i) \quad \mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} = \cdots = \mu_2^{(P)}$$

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$$\mu_c^{(1)} = \mu_c^{(2)} = \mu_c^{(3)} = \cdots = \mu_c^{(P)}$$

For each component, we have (P-1) eqn and thus for 'c' components, the no. of eqn will be c(P-1)

Therefore, the degree of freedom or the number of independent variables F is given by

F = Total number of variables – Total number of relations among the variables

$$= PC + 2 - P - c(P-1)$$

$$= P\cancel{C} + 2 - P - \cancel{cP} + c$$

$$\boxed{F = c - P + 2} \quad \cdots\cdots \quad (ii)$$

Eqn(ii) is the phase rule which relates the number of phases and components with the variance of the system.

Examples:

1. Calculate the number of components and degrees of freedom for the following equilibria

i) An aqueous solution of glucose.

Ans. Since the system is non-reactive, the no. of components = No. of chemical species = 2 (water and glucose)

Since P = 1, hence, $F = c - P + 2 = 2 - 1 + 2 = 3$

(temp, pressure, concn of soln)

(iii) An aqueous solution of Nacl.

Ans. $C = 2$ (Nacl and water)

$P = 1$

$F = C - P + 2 = 2 - 1 + 2 = 3$ (Temp, pressure, concn.)

2. Calculate the number of components, phases, degrees of freedom of the system —

i) A liquid at its critical temperature.

Ans. At the critical point, the liquid phase and vapour phase become indistinguishable. This places a restriction on the variance of the system. Thus at the critical point of a liquid,

$C = 1$; $P = 2$;

$F = \cancel{1} - \cancel{2} + \cancel{2} - 1 = 0$.

Thus, the critical point of a liquid is invarian

ii) A binary azeotrope.

* The composition of the liquid phase is equal to the composition in the vapour phase and hence, a restriction on the variance of the system. Thus,

$C = 2, P = 2$

and one restriction due to the identical composition of the liquid and vapour phase.

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

Clapeyron Equation:

From thermodynamics, we know that for any pure substance in a single phase, such as, liquid or gaseous water, the variation in free energy is given by

$$dG = V\,dp - S\,dT \quad \text{-----} \quad (i)$$

For a pure substance present in two phases A and B at a pressure P and temperature, T the condition of equilibrium is

$$\overline{G}_B = \overline{G}_A$$

$$\text{or,} \quad \Delta G = 0 \quad \text{- - - - - - - - -} \quad (ii)$$

Where $\overline{G}_A$ is the free energy per mole of the substance in the initial phase A and $\overline{G}_B$ is the free energy per mole in the final phase B.

If the temperature of the system is changed to T+dT, then the pressure of the system will change to P+dp to maintain the equilibrium. The relationship between dT and dP can be derived from thermodynamics as—

Let the free energy per mole of the substance in phase A at the new temperature and pressure be $\overline{G}_A + d\overline{G}_A$ and that in phase B be $\overline{G}_B + d\overline{G}_B$. Since the two phases are still in equilibrium, hence

$$\overline{G}_A + d\overline{G}_A = \overline{G}_B + d\overline{G}_B \quad \text{- -} \quad (iii)$$

According to eqn. (i), $d\overline{G}_A = V_A\,dP - S_A\,dT$ - - (iv)

and $d\overline{G}_B = V_B\,dP - S_B\,dT$ - - - - - (v)

Since $\overline{G}_A = \overline{G}_B$

Hence, from eqn. (iii) $d\overline{G}_A = d\overline{G}_B$ - - - (vi)

$$V_A\,dP - S_A\,dT = V_B\,dP - S_B\,dT \quad \text{- - -} \quad (vii)$$

$$\text{or,} \quad \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}$$

$$\text{or,} \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad \text{- - - - - - - - - -} \quad (viii)$$

~~Eqn. (viii) is~~ where ΔS and ΔV are the change in entropy and volume respectively. when 1 mole of the substance passes from the initial phase A to be final phase B.

If 'q' is the heat exchanged reversibly per mole of the substance during the change of phase at temperature T, then the change of entropy (ΔS) in this process is given by $\Delta S = \frac{q}{T}$.

Hence, $$\frac{dP}{dT} = \frac{q}{T.\Delta V} \quad \text{-----(ix)}$$

or, $$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)} \quad \text{----(x)}$$

The eq^n (x) is known as <u>Clapeyron Equation</u> and given change in pressure accompanying the change in temperature dT or vice versa when two phases of a pure substance are in equilibrium with each other.

Clausius - Clapeyron Equation :

The Clapeyron equation, when applied to the liquid-vapour or solid-vapour equilibrium, with the assumption that the volume of the liquid and solid phase is negligible as compared to vapour phase which behaves as an ideal gas, is called the Clausius - Clapeyron equation.

If the temperature is not too near the critical temperature, then $V_g >> V_l$ or, V_s

and $V_g = \frac{RT}{P}$

With this simplification we can write from eq^n (x),

$$\frac{dP}{dT} = \frac{\Delta H}{T V_g} = \frac{\Delta H}{T} \times \frac{P}{RT} = P \frac{\Delta H}{RT^2}$$

$$\therefore \frac{dP}{P_1} = \frac{\Delta H}{R} \frac{dT}{T^2} \quad \text{-----(xi)}$$

[$q = \Delta H$ = molar heat of vaporisation]

This differential equation may be employed if the changes in temperature and pressure are small.

Integrated Form of Clausius – Clapeyron Equation:

Assuming that ΔH (molar enthalpy of vaporization / molar enthalpy of sublimation) remains constant to small temperature variations, integration of equation (xi) yields,

$$\int \frac{dP}{P} = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\text{or, } \ln P = -\frac{\Delta H}{R} \cdot \left(\frac{1}{T}\right) + c \qquad \text{- - - (xii)}$$

$$\text{or, } \log P = -\frac{\Delta H}{2.303 R} \left(\frac{1}{T}\right) + c' \qquad \text{- - - (xiii)}$$

where c and c′ are integration constants.

$$\text{Again, } \int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\text{or, } \ln \frac{P_2}{P_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\text{or, } \ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad \text{- - - - (xiv)}$$

If ΔH is known, vapour pressure at a desired temperature can be calculated from the knowledge of single value of vapour pressure at a given temperature.

Numerical Problems:

1. At 373.6 K and 372.6 K the vapour pressures of water are 1.018 and 0.982 atms respectively. Calculate the heat of vapourisation of water.

Ans. $T_1 = 372.6 K$ $\qquad R = 8.314 \ JK^{-1}$

$T_2 = 373.6 \ K$ $\qquad \Delta_v H = ?$

$P_1 = 0.982$ atm

$P_2 = 1.018$ atm

According to Clausius - Clapeyron equation,

$$\log \left(\frac{P_2}{P_1}\right) = \frac{\Delta_v H}{2.303 R} \times \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\text{or, } \log \frac{1.018}{0.982} = \frac{\Delta_v H}{2.303 \times 8.314} \times \frac{1}{372.6 \times 373.6}$$

$\Delta H = 41676.13 \text{ J/mol}$

$= 41.676 \text{ KJ/mol}$

Phase Transition:

Many substances exist in more than one solid forms differ~~ent~~ing in crystal structures which are quite stable thermodynamically over certain range of temperature and pressure. This phenomenon is called polymorphism. In the case of elements, this property of polymorphism is called allotropy. Due to change in T and P, one form (phase) may change or undergoes transition into the other form. This process in which a new phase appears without taking place of a chemical reaction is called phase transition.

a) First-order Phase Transitions:

These are the transitions which are accompanied by transfer of heat between the system and the surroundings ($q_p \neq 0$). The heat capacity $C_p = \left(\frac{\partial H}{\partial T}\right)_P$ may be +ve or -ve. during transition from low temperature phase to high temperature phase. Since, at the equilibrium transition temperature, latent heat is involved. without change of temperature, $C_p = \frac{dq_p}{dT}$ is infinite. Further, in these transitions, there is change in the enthalpy and volume of the system, i.e., $\Delta V \neq 0$, $\Delta H \neq 0$.

Eg, $\text{ice}(s) \overset{273K}{\rightleftharpoons} H_2O(l)$, $\Delta C_p = +ve$, C_p at $273K = \infty$

$H_2O(l) \rightleftharpoons \underset{\text{(stream)}}{H_2O(g)}$, $\Delta C_p = -ve$, C_p at $373K = \infty$

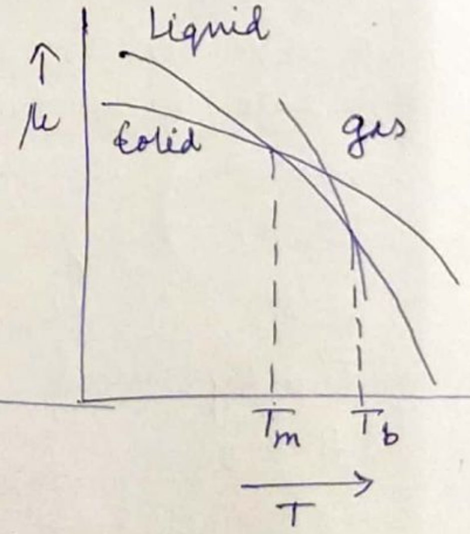
The clapeyron equation is applicable to the first order transitions.

In the first order transitions, there is change in the Gibbs free energy and a finite change in the volume and entropy at constant pressure. Since the latter quantities are first derivatives of the free energy, such transitions are accompanied by discontinuity in the first derivatives, i.e., the slopes of the plots of μ against P or T are different on either side of the transition. Also, $\left(\frac{\partial \mu}{\partial T}\right)_P = -\bar{S}$ and $\bar{S}$ of a pure substance is always +ve about 0 K, therefore, 'μ' of each phase decreases with increasing T.

Further, $S_{(g)} > S_{(l)} > S_{(s)}$ so that,

$$\left(-\frac{\partial \mu}{\partial T}\right)_{gas} > \left(-\frac{\partial \mu}{\partial T}\right)_{liq} > \left(-\frac{\partial \mu}{\partial T}\right)_{solid}$$

The change of μ of the solid, liquid and gas phase of a pure substance with temperature at constant pressure can be shown in the figure. Tm is the melting point and T_b is the boiling point of the substance.



Variation of μ with T in first order phase transition at eqlm of pure substance at constant pressure.

★ 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 — (two phases)

i) Liquid ⇌ vapour

ii) Solid ⇌ vapour

iii) Solid ⇌ liquid

The 1 three phase eqm is —

solid ⇌ liquid ⇌ ~~ga~~ vapour

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 eqm, the degrees of freedom,

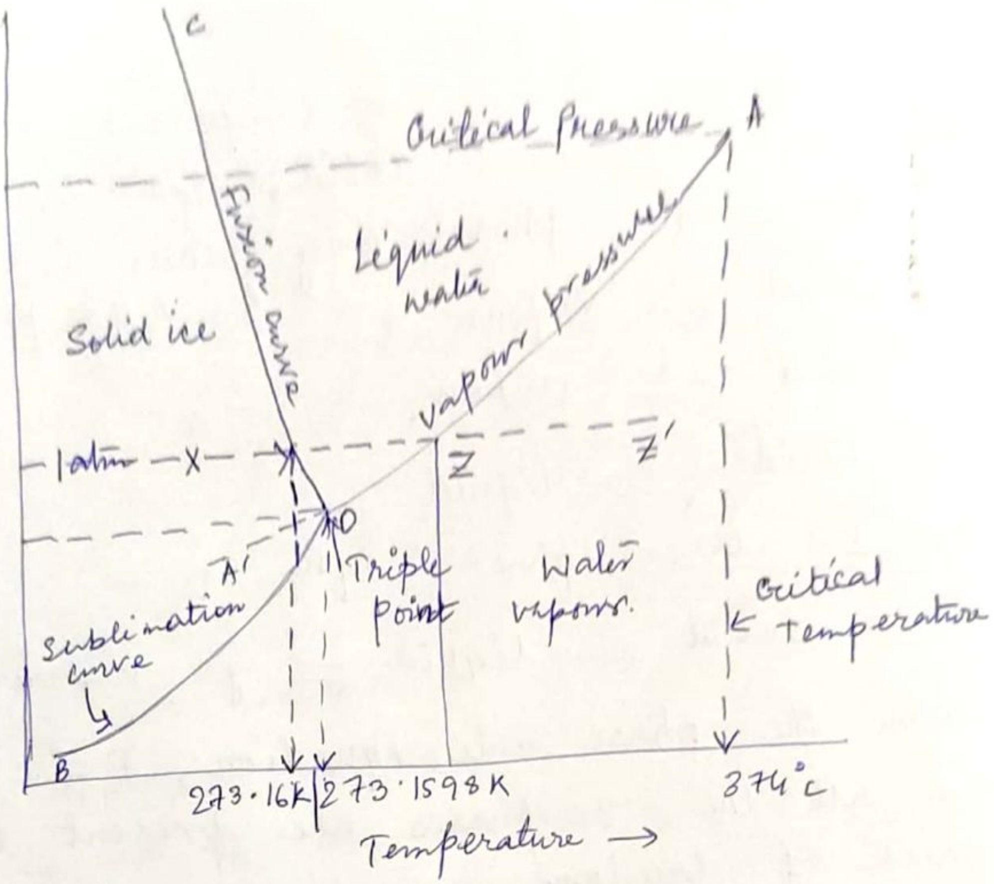
$$F = c - P + 2 = 1 - 2 + 2 = 1.$$

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 eqm.



Curve OA:

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

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

Curve OB:

It repreamts the eqlm between ice and vapours at different temperatures. It is called the sublimatio 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 slop of the curve is (+) ve.

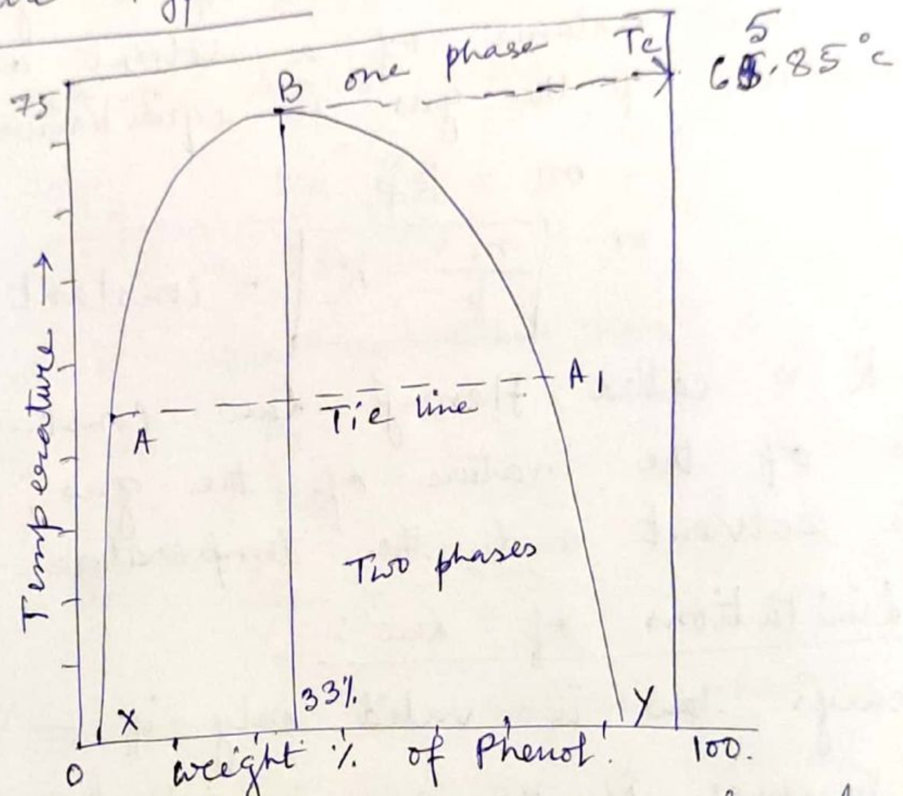
Curve OC: This curve represents the eqlm betwe ice and liquid water. It is called the fusion curv of ice. The slop of this curve is (–) ve.

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

i) Minimum boiling azeotropes: Eg → water and ethyl alcohol
(show (+)ve deviation)

ii) Maximum boiling azeotropes: (−) ve deviations from ideal behaviour. Eg → a mixture of H_2O 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 complete miscible. In other words, at ~66°c and above, phenol and water are completely miscible in all proportions and yield only a single layer on mixing.

(iii) 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 eqbm with A.

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

(v) The domed-shaped area represents the two phases in eqbm 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 corresponds to the maximum point of the curve, it is termed upper critical solution temperature (UCST).