Phase Rule

1. State the Phase rule and explain the terms in it.

A. W Gibbs deduced an equation by using the principles of thermodynamics which is known as phase rule equation. It is applicable to all heterogeneous systems in equilibrium.

Def : " The number of degrees of freedom and the number of phases of a system exceeds the number of components of that system by two".

Mathematically $F + P = C + 2$

(or) $F = C - P + 2$

F is the number of degrees of freedom
C is the number of components
P is the number of phases.

Phase (P) : " The homogeneous parts of a heterogeneous system in equilibrium, which are physically distinct and mechanically separable are known as phases.

Ex : (i) A mixture of two or more gases ; a mixture of two (or) more miscible liquids are homogeneous. In such systems, $P=1$ Ex : Air

(ii) Two immiscible liquids, solid + gas ; solid + liquid , liquid + gas and two solids constitute two different phases

(iii) In the water system, we have 3 phases namely Ice, water and Vapour.

Components (C) : " The minimum number of independently variable constituents by means of which the composition of each phase present in the system can be expressed either directly (or) in the form of a chemical equation in which zero (or) negative values are permissible.

Ex : (i) Water system has 3 phases i.e, Ice (solid) , water (liquid) and water vapour (gaseous). The composition of all the three phases is expressed in terms of one chemical compound, H_2O. Thus the water system has only one component.

(ii) $$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

It is a two component system since atleast two out of the three constituents are required to represent the composition of all 3 phases. If $CaCO_3$ and CO_2 are selected as components

$$CaCO_3 \longrightarrow CaCO_3 + 0\,CO_2$$
$$CaO \longrightarrow CaCO_3 - CO_2$$
$$CO_2 \longrightarrow 0\,CaCO_3 + CO_2$$

Similarly CaO and CO_2 (or) $CaCO_3$ and CaO are choosen as components.

Degrees of Freedom (F) : " The minimum number of the variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily fixed in order to define condition of the system completely is termed as degree of Freedom of the system

Ex: (I) A gaseous mixture of two gases is a system with three degrees of freedom i.e, it is trivariant

From phase rule, $F = C-P+2 = 2-1+2 = 3$

(ii) For the system water in equilibrium with its vapour, temperature is the only quantity which has to be fixed. So it has one degree of freedom i.e, it is Univariant.

From phase rule, $F = C-P+2 = 1-2+2 = 1$

(iii) The system of Ice - water - vapour in equilibrium has no degree of Freedom.

$$Ice_{(s)} \rightleftharpoons water_{(l)} \rightleftharpoons Vapour_{(g)}$$

It is In-Variant

From phase rule, $F = C-P+2 = 1-3+2 = 0$

Q. What is a one Component System? Explain the phase diagram of water system.

Ans. one Component System: If all the constituents (phases) present in a System are expressed in terms of only one chemical compound, then it is known as a one component system.

Water System is a one component System since all the 3 phases namely Ice, water and Vapour are expressed in terms of H_2O. The phases are present in equilibrium as

(i) $water_{(l)} \rightleftharpoons Vapour_{(g)}$

(ii) $Ice_{(s)} \rightleftharpoons Water_{(l)}$

(iii) $Ice_{(s)} \rightleftharpoons Vapour_{(g)}$

(iv) $Ice_{(s)} \rightleftharpoons water_{(l)} \rightleftharpoons Vapour_{(g)}$

The no. of Phases that exist in equilibrium at any time depends upon the condition of pressure and temperature. These conditions have been determined experimentally. After ploting these on graph paper by taking pressure and temperature on appropriate axis we get a phase diagram.

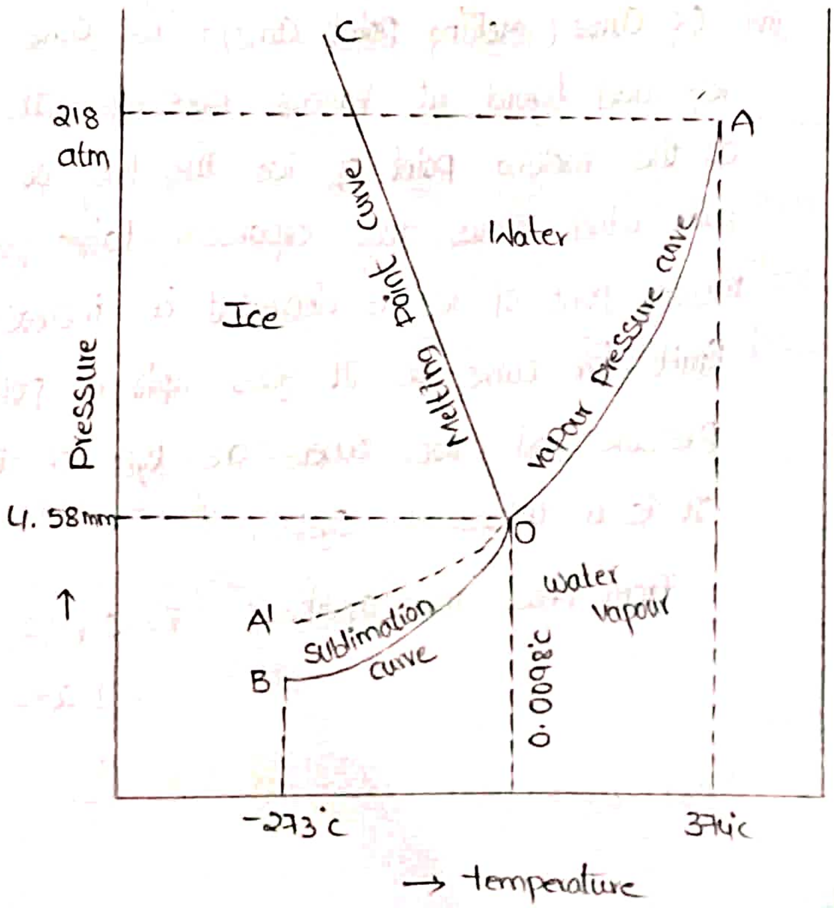
The phase diagram has

(i) stable curves
OA, OB & OC.

(ii) one metastable curve OA'

(iii) Three areas
AOC, BOC & AOB

(iv) Triple point 'O'



Curves :

(i) OA (Vapourisation Curve) : This is the vapour pressure curve of water. It represents the equilibrium between water and Vapour at different temperatures The curve starts at point 'O' which is the freezing point of water. The curve ends at A (374°C at 218 atm) , the critical temperature beyond which the two phases merge into each other. It is univariant. From phase rule equation, $F = C-P+2 = 1-2+2 = 1$

(ii) OA' curve : The dotted curve OA' is a continuation of the OA curve and represents the vapour pressure curve of Supercooled water. This curve is known as metastable curve. When slight disturbance is there, the supercooled water changes to Ice and the curve merges into OB.

(iii) OB Curve (Sublimation Curve) : It is the vapour pressure curve of Ice It gives various values of temperature and pressure at which ice and water vapour co-exist. It is obtained by studying the effect of pressure on freezing point of water. The curve starts from point O and ends at B (-273°C) . It has one degree of freedom. From phase rule equation,

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

(iv) OC Curve (Melting point curve) : The curve shows the equilibrium between ice and liquid at various pressures. It shows the effect of pressure on the melting point of ice. The line OC inclines towards the pressure axis which shows that expansion takes place on freezing of water and melting point of ice is decreased by increase of pressure. There is no limit for curve OC It goes upto a point corresponding to 2000 atm pressure and -20°C, where one type of ice changes into another solid. It is a univariant system.

From phase rule equation, $F = C-P+2$

$$= 1-2+2$$

$$= 1$$

Areas : In water system, there are three areas

Area AOB consists of water vapour only

Area BOC consists of ice only

Area COA consists of water only

According to phase rule equation, $F = C - P + 2 = 1 - 1 + 2 = 2$

so these areas are bivariant i.e., for locating any point in these areas, both temperature and pressure must be fixed.

Triple Point (O) : It is the point where the three curves OA, OB and OC meet together. At this point, all the three phases Ice, water and vapour are in equilibrium. At point 'O', temperature and pressure are fixed at 0.0098°c and 4.58 mm respectively. One of the three phases disappear, when either pressure or temperature is changed. So the system has zero degree of freedom (in-variant system).

From phase rule equation, $F = C - P + 2$

$= 1 - 3 + 2 = 0$.

3. Explain the phase diagram of Ag-Pb system.

A. Silver-Lead System : It is a two component system, the two components being silver and lead. The possible phases are (i) solid Ag (ii) Solid Pb (iii) Solution of Ag and Pb in molten state and (iv) vapour.

Since the boiling points of silver and lead are considerably high, the vapour phase is practically absent and thus the silver-lead system consists of only solid and liquid phases, the number of degrees of freedom reduced by one.

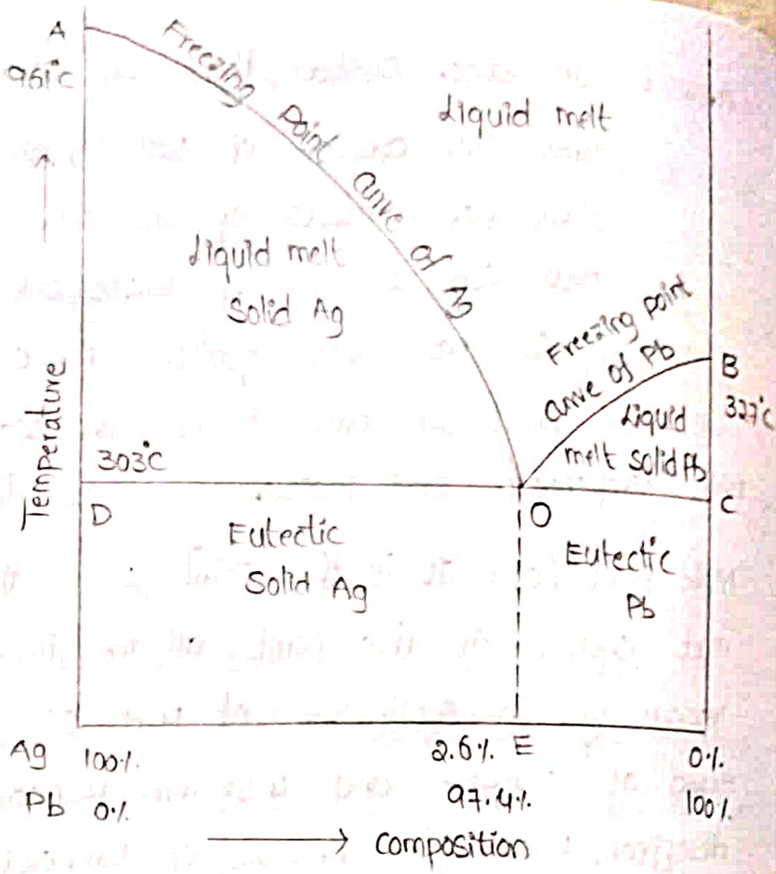
The reduced phase rule equation is $F' = C - P + 1$

The phase diagram of the system consists of

(i) Curves OA and OB

(ii) Eutectic point O

(iii) Areas AOD, BOC, DOE, COE and area above curve AOB



Curves:

(i) AO curve: It represents the melting point of various mixtures of silver obtained by the addition of Pb to pure Ag. Since the addition of metal to another pure metal lowers the melting point of the latter, the curve AO is also refered to as the freezing point curve of Point A represents the melting point of the pure silver (961°c)

All along the curve AO; the added metal pb gives into the solution and the separation of the original metal Ag occurs till the point O is reached. At the point O no more lead goes into the solution because at this point the solution becomes saturated with the added metal and hence the melting point of Ag does not fall further.

All along the curve AO, two phases solid Ag and melt of the two metals are present in equilibrium. So according to reduced phase equation the system is univariant.

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

$$= 2-2+1 = 1$$

(ii) BO Curve : It represents the melting points of various mixture of lead obtained by the addition of silver to pure pb. It is also referred to as the freezing point curve of lead. Point B represents the melting point of pure lead (327°c).

All along the curve BO, the added metal silver goes into the solution and the separation of the original metal lead occurs till the point O is reached. At point 'O', no more Ag goes into the solution because at this point the solution becomes saturated with the added metal and hence the melting point of lead does not fall further.

All along the curve BO, two phases solid Pb and melt of the two metals are present in equilibrium. so it is univariant.
From reduced phase rule equation , $F' = C-P+1 = 2-2+1 = 1$.

Eutectic point 'O': This is the point where the two curves AO and BO meet together. At this point three phases (solid Ag, solid pb and their liquid solution) co-exist. Therefore, point O has no degree of freedom i.e., it is invariant.

According to reduced phase rule equation

$$F' = C-P+1 = 2-3+1 = 0$$

The point O represents the lowest possible temperature (303°c) at which liquid phase can exist and beyond which the liquid phase cannot be enriched in either component by freezing out the other component. Such a point 'O' is called the Eutectic point. The temperature (303°c) and composition of the components (2.6% Ag + 97.4% Pb) corresponding Eutectic mixture respectively.

Areas :

The area above the curve AOB consists only one phase i.e melt of Ag and pb. So it has two degrees of freedom.
The area AOD has two phases namely solid silver and liquid melt.

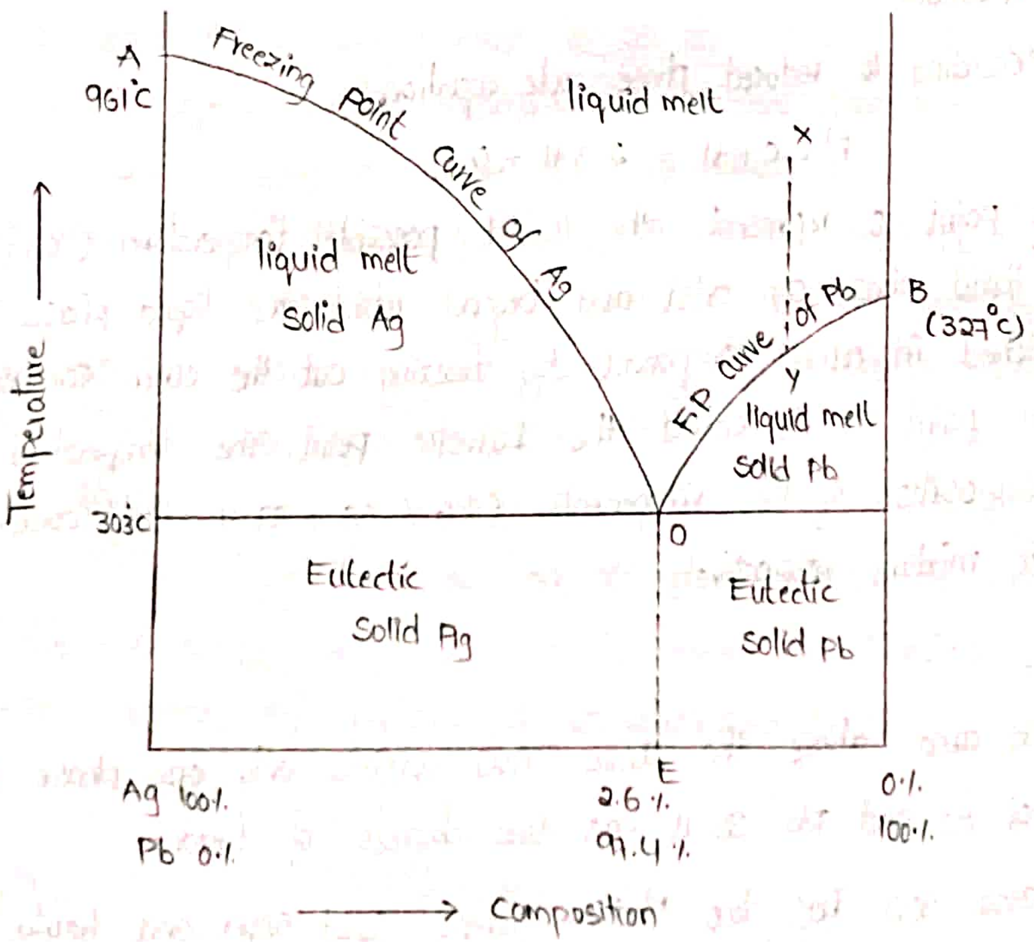
The area BOC has two phases namely solid lead and liquid melt
The area DOE has two phases namely solid silver and Eutectic
and the area COE has two phases namely solid lead and Eutectic.

Systems in these areas have one degree of freedom (i.e, univariant)
From reduced phase rule equation,

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

4. Write the application of silver-lead system

Ans: Galena (PbS) is usually associated with silver. During the extraction of lead from galena, a very small amount of silver (less than 0.1%) remains associated with lead because silver is soluble in lead to some extent. The lead thus obtained is known as argentiferous lead. The process of removing the traces of silver from argentiferous lead is known as desilverisation of lead and is based on the phase diagram of silver-lead system.



The argentiferous lead is heated to a temperature well above its melting point so that the system consists only of liquid phase Let the point x represents the system "molten lead" on the phase diagram It is then allowed to cool The temperature of the melt will fall along the line xy without any change in the concentration till the point y is reached As soon as the point y is reached; lead will begin to crystallise out and the solution will contain relatively increasing amount of silver Further cooling will shift the system along the line yo Lead continues to separate out and is constantly removed by means of ladels Thus the melt continues to be richer and richer in silver till the Eutectic point 'O' is reached where percentage of silver increases to 2.6%. This alloy containing 2.6% Ag and 97.4%. Pb is treated for the recovery of silver profitably.

This principle of increasing the relative proportion of silver in the alloy is known as pattison's process and is commercially used for desilverisation of lead

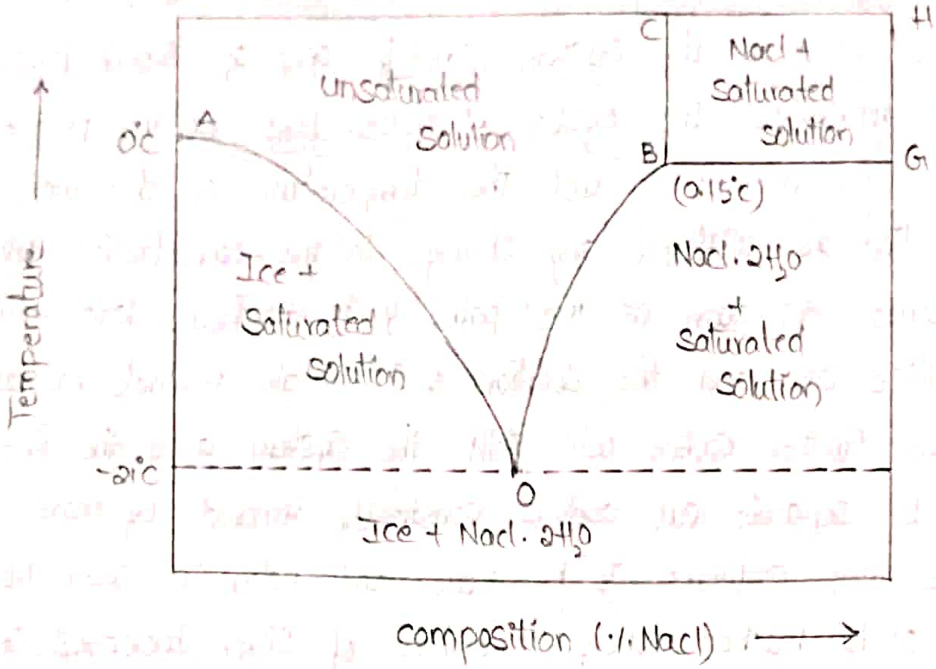
Systems having congruent melting points:

A system (compound) is said to process congruent melting point, if it melts sharply at a constant temperature, having the same composition as in solid state

Examples for systems having congruent melting point are Zinc - Magnesium system, Gold - Tin system, Ferric chloride - water system, Phenol - Aniline system etc,

5. Explain the phase diagram of NaCl - H_2O system.

Ans: Salt - water system: It is a two component system Neglecting the vapour phase, the system exhibits four phases (i) NaCl (ii) ice (iii) Solution and (iv) NaCl $2H_2O$



The temperature - composition diagram of the system consists of

(i) AO curve: It is known as the freezing point curve of water. Point A is the melting point of ice (or freezing point of water) which is 0°c at 1 atm pressure. When NaCl is added to water, its freezing point is lowered. This takes place till point O is reached after which addition of NaCl does not lower the freezing point further. Along this curve two phases ice and solution are in equilibrium. Therefore, system along the curve is univariant.

From reduced phase rule equation,

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

(ii) OB curve: It is known as the solubility curve of the hydrated sodium chloride. When further amount of sodium chloride is added at point O and the system is heated, ice disappears. The curve OB represents the effect of temperature on the solubility of the hydrated sodium chloride, $NaCl.2H_2O$. The steep rise of the curve OB shows that the solubility of sodium chloride increases with rise in temperature.

Along this curve two phases ($NaCl \cdot 2H_2O$ and solution) are in Equilibrium so the system is univariant

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

The point B (0.15°c) represents, the incongruent melting point of the dihydrate where anhydrous sodium chloride appears

(iii) BC curve: It is the solubility curve of the anhydrous sodium chloride Along this curve two phases (NaCl and solution) exist together. Hence the system along the curve is univariant. $F' = C-P+1 = 2-2+1 = 1$

(iv) Point O: At point 'O' the solution becomes saturated and the dihydrate, $NaCl \cdot 2H_2O$ separates out. Thus the system at the point 'O' consists of three phases namely ice, $NaCl \cdot 2H_2O$ and solution are in equilibrium. Solid as well as solution phase at this point contains 23% NaCl. The temperature at this point (-21°c) is the lowest temperature that can be attained in the System. This point is called the Eutectic point. Since three phases exist at this point, the system is invariant.

$$F' = C-P+1 = 2-3+1 = 0$$

System having incongruent melting point:

A System (compound) is said to posses incongruent melting point, if it decomposes much below its melting point and forms a new solid phase and a solution having different composition from solid state. It has no sharp melting point.

original solid $\rightleftharpoons$ New solid + solution (melt)

The decomposition at this temperature is known as Peritectic reaction and the temperature (incongruent melting point) is known as peritectic temperature

Ex: $NaCl - H_2O$ System, sodium- potassium System, gold- antimony System