PHASE RULE

Definitions

Phase rule : For any system in phase equilibrium at definite temperature and pressure, the number of degrees of freedom F of is related to the number of components C and phases P by the phase rule equation **$F = C - P + 2$**

Phase P: A homogeneous , physically distinct and mechanically separable portion of a system in phase equilibrium is called a phase.

Ex: ice $\rightleftharpoons$ water $\rightleftharpoons$ water vapour consists of three phases.

Glucose solution consists of only one phase.

Component C: The smallest number of independent constituents by means of which the composition of each phase can be expressed in the form of a chemical equilibrium

Ex : 1. ice $\rightleftharpoons$ water $\rightleftharpoons$ water vapour

In this equilibrium three phases present, but all are made of one chemical, H_2O molecule. Hence number of components is one. (one component system)

2. Glucose solution consists of only one phase but the composition can be expressed in terms of the amounts of glucose and water. So, it is a two component system.

Degrees of freedom F: It is the number of independent variables such as temperature T, pressure P, volume V, composition etc, which must be specified in order to represent the condition of a system at equilibrium

Applications of Phase Rule

1. One component system.

Water can exist in three phases viz ice, water and vapour.There can be three forms of equilibria

1. water $\leftrightarrow$ water vapour 2. Ice $\leftrightarrow$ water vapour 3. Ice $\leftrightarrow$ water.

Since H_2O is the chemical component involved in three phases, it is a one component system.

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

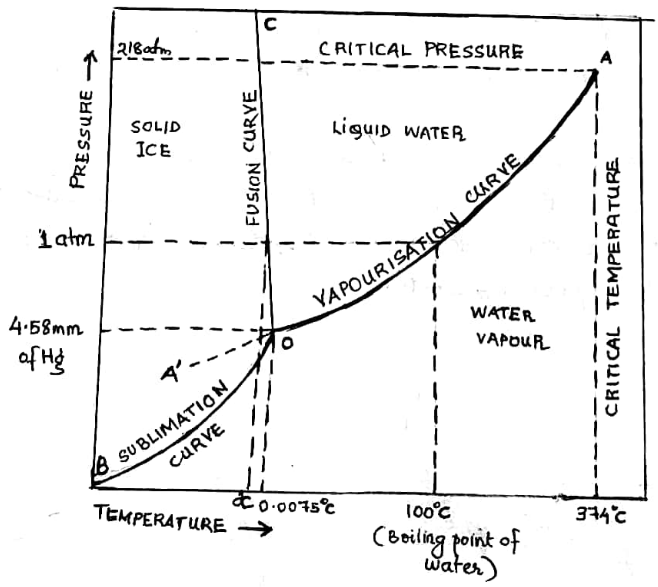
the number of degrees of freedom required are

1.When P=1, F= 2 (bivariant) ; 2. When P=2, F=1 (univariant); 3. When P=3 , F=0 (invariant)

the maximum number of degrees of freedom is two. Such a system can be represented by a two dimensional diagram. The convenient variables are the pressure and the temperature.

The water system

The phase diagram for water system is shown below.



Areas: BOC represents the solid phase ice, AOC represents the existence of liquid water and the area BOA is the region where vapour phase exist at various temperatures and pressures. Within these single–phase areas, according to phase rule C=1 ,P=1 and hence F= 1– 1 +2 = 2 ; the system is bivariant, ie. to locate any point in the area, both temperature and pressure need to be known. For example at a given temperature (say 1atm), ice exists at different pressures (-5^{0}C or -10^{0}Cor -25^{0}C) and vice versa.

Curve OA- vapour pressure curve along which the equilibrium between liquid water and vapour at different temperatures exist. The degrees of freedom is F=C– P +2 = 1 – 2+2 =1, system is univariant along the curve. Thus if temperature is given the equilibrium pressure can be determined.ie. To locate any point on the curve, only one variable either temperature or pressure is needed. At 100^{0}C the vapour pressure equals the atmospheric pressure, therefore is the boiling point of water. Curve OA extends up to 374^{0}C which is the critical temperature of water above which liquid water can not exist and critical pressure is 218 atm. Only water vapour exist above this point. It is the critical point of water.

Curve OB- sublimation curve represents the equilibrium between ice and vapour at different temperatures and pressures. It extends upto –273^{0}C at which ice merge into vapour. F=C– P +2 = 1 – 2+2 =1, system is univariant along the curve.

Curve OC- fusion curve: Along this curve equilibrium between ice and liquid water exist and also called as melting point curve of ice.This curve shows the effect of pressure on the melting point of ice. OC is inclined towards the pressure axis, which indicates that the melting point of ice is lowered by increase of pressure. F=C– P +2 = 1 – 2+2 =1, system is univariant along the curve.

Triple point O: At this point O where curves OA,OB and OC meet together. Three phases solid ice , liquid water and water vapour coexist. Such a point is known as the **triple point**. For water, the temperature and pressure at the triple point is 0.0075^{0}C and 4.58mm of Hg respectively. According to phase rule triple point is an invariant point F= C – P +2, =1- 3+2= 0. ie. neither pressure or temperature can be altered. Slight variation in either of it causes the disappearance of one of the three phases.

Metastable equilibrium: The dotted **Curve OA'** represents the vapour pressure curve of supercooled water. It is obtained on cooling the water carefully without stirring in a clean and smooth vessel. The liquid is in equilibrium with vapour state. It is called super cooled water and is said to be in a metastable equilibrium state because a slight disturbance or a small particle of ice cause this water to solid ice immediately.

PHASE RULE FOR TWO COMPONENT SYSTEMS

When there are two components, C=2, applying phase rule the degree of freedom F will be: When P=1, F= 2-1+2 =3, when P=2; F= 2,and when P=3; F=1. F has the highest value 3 when P=1. So phase study of a two component system may be represented by a three –dimensional diagram of pressure, temperature and composition, which cannot be shown on a paper.

When we consider only solid-liquid equilibrium; vapour phase may not be considered. Then effect of pressure is very small on this type of equilibrium. Thus experiments can be conducted under atmospheric pressure (constant pressure). Such a system is called **condensed system** and we may apply

reduced phase rule equation F = C – P + l

For solid –liquid equilibria, two cases arises

The two components are miscible in liquid state 2. The two components are partially miscible in liquid state. We shall restrict to the first case. Under this first category, three cases arise.

a)Simple eutectic systems. b).Two component systems with congruent melting point.

c).Two component systems with incongruent melting point .

1. **Simple Eutectic system**

A binary system consisting of two substances which are miscible in all proportions in the liquid phase, but do not react chemically is known as the **simple eutectic system.** Each component lowers the freezing point of the other component

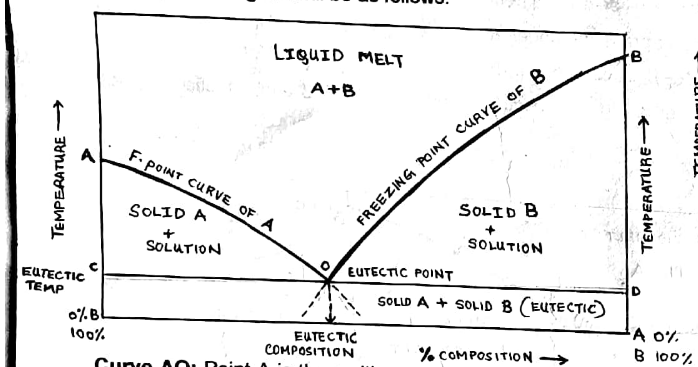
Eutectic mixture is a solid solution of two or more substances having the lowest freezing point of all the possible mixtures of the components.

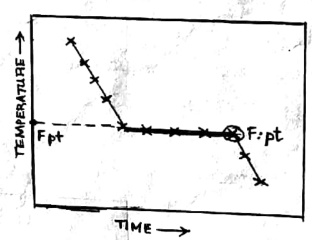
Eutectic point : The minimum freezing point attainable by a two component system corresponding to the eutectic mixture is known as the eutectic point.

General Phase diagram of simple Eutectic system

The Since measurements are made at atmospheric pressure **condensed phase rule** or **reduced phase rule equation** $F = C - P + 1$ will be applicable.

General phase diagram will be as follows.





COOLING CURVE TO DETERMINE FREEZING POINT

Curve AO: Point A is the melting point (or freezing point) of pure component A. As increasing quantities of B are added to A, the freezing point of A falls along the curve OA till the lowest freezing point O is reached. Melting point does not fall any further at O. Further addition of B separates it as solid phase. AO is the freezing point curve of component A.

Along AO solid A is in equilibrium with solution of B in A. The composition of B in A varies with temperature along AO. The system is F =2-2+1= 1 univariant along OA

Curve BO: Point B is the melting point (or freezing point) of pure component B. As increasing quantities of A are added to B, the freezing point of B falls along the curve OB till the lowest freezing point O is reached when the solution gets saturated w.r.t. B. BO is the freezing point curve of component B with varying compositions of A. Along BO solid B is in equilibrium with solution of A in B.The system along the curve BO is F =2-2+1= 1 univariant like AO.

Eutectic point O: The two curves AO and BO meet at O, where three phases solid A,solid B and their solutions coexist and the system is invariant F = 2-3+1 = 0 This point is called Eutectic point. This is the lowest melting point (freezing point)of the mixture. This temperature is called **eutectic temperature** and the composition is called the **eutectic composition**. At O, the temperature remain constant until the whole melt solidifies.

Area AOB: represents solution of A and B. only liquid exist. System is F = 2-1+1= 2 bivariant

Area AOC : solid A is in equilibrium with solution of varying composition of B in A depending upon the temperature.

Area BOD : solid B is in equilibrium with solution of varying composition of A in B depending on temperature.

Area under CD: Ultimately , the solution phase solidifies into the area under CD where the coexistence of two solids A and B.

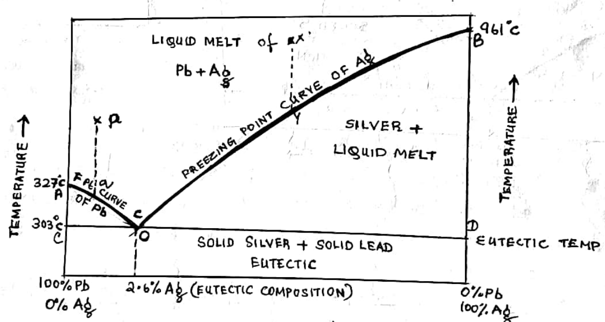
1. Lead- Silver System

Applying phase rule, the degree of freedom F will be: When P=1, F= 2-1+2 =3, when P=2; F= 2,and when P=3; F=1. F has the highest value of 3 when P=1. So phase study requires three variables which may be represented by a three –dimensional diagram of pressure, temperature and composition. This cannot be shown on a paper.

Gaseous phase is almost absent in this equilibrium and hence influence of pressure can be neglected. The experiment can be conducted at constant pressure (under atmospheric pressure) and **reduced phase rule equation F = C – P + I** can be applied.

Melting point of Lead is 327^{o}C and Silver is 961^{o}C. Eutectic temperature is 303^{o}C and eutectic composition is 2.6% Ag and 97.4% Pb

Phase Diagram



Curve OA is the freezing point curve of Lead. Point A (327^{o}C) is the freezing point (melting point) of lead. The melting point gradually falls along AO on addition of small quantities of silver till the lowest freezing point O is reached. At this point solution is saturated w.r.t silver and melting point of lead will not fall anymore. Along AO solid lead is in equilibrium with solution of silver in lead. The system is F =2-2+1= 1 univariant along OA

Curve BO: is the melting point (or freezing point) curve of silver. Point B (961^{o}C) is the melting point (or freezing point)of pure component silver. As increasing quantities of lead are added to silver, the freezing int of silver falls along the curve BO till the lowest freezing point O is reached. The solution gets saturated w.r.t. lead. Along BO solid silver is in equilibrium with solution of lead in silver. Along the curve BO, F =2-2+1= 1, the system is univariant like AO. On further cooling, the whole system crystallizes out.

The point O is called the <u>eutectic point.</u> The temperature at O (303^0C) is the <u>eutectic temperature</u>. The composition of two components at this point is 2.6% Ag and 97.4% Pb and is known as <u>eutectic composition.</u>

Mixture of lead and silver has the lowest melting point at this point. Temperature remains constant until the whole solution become solid.

Areas: Two regions exist below eutectic temperature. In one region solid Ag and solid eutectic are present while the other region contains solid Pb and solid eutectic.

Area AOB: In this region solution of various compositions of lead and silver exist.

AreaAOC: Within this region pure solid Pb and liquid of given composition are in equilibrium

AreaBOD: Pure solid Ag and liquid of given composition are in equilibrium

Effect of cooling a liquid mixture : Let us consider a liquid at 'x' On cooling it remains as liquid till to point 'y' and at 'y' pure Ag crystallizes out. This point is the freezing point of Ag –Pb alloy of that composition. As cooling continues the temperature will fall along BO, more and more Ag crystallize out till the eutectic point is reached.

If we take a solution of composition 'p' is taken and allowed to cool similar events occurs but Pb crystallizes at 'q' and on further cooling more and more Pb crystallizes out.till eutectic composition is reached.

This phase diagram of Lead –Silver system has special significance with <u>desilverisation of Lead.</u>

When Argentiferous Lead containing small% of silver (say 1%) is first heated to a temperature above its melting point, say by point 'p' in figure. It is then allowed to cool, the temperature will fall along 'pq'. At 'q' ,Lead will begin to crystallize out and it is removed. The remaining solution will contain increasing amount of silver.Further cooling will shift the system along the curve 'qO' and lead continues to separate out and is constantly removed. The solution thus continues to be richer and richer in silver until point 'O' is reached where % of silver rises to 2.6%. This method is used in alloy making process and is known as **<u>Pattinson's process of desilverisation of lead.</u>**

Some other eutectic systems.

1. **Lead- Antimony eutectic system**

   Lead – meltin point 327^0C

   Antimony- melting point 631^oC

   Eutectic temperature 246^oC

   Eutectic composition 87% lead and 13% antimony

2. **Bismuth – Cadmium Eutectic system**

   Bismuth – meltin point 273^0C

   Cadmium- melting point 323^oC

   Eutectic temperature 140^oC

   Eutectic composition 40% Cd and 60% Bi