

# Phase Equilibrium

## Introduction :

Two or more different phases present in equilibrium with one another, constitute **a heterogenous** system. Such heterogenous system can be conveniently studied with the help of a generalization called **Gibbs Phase** rule. It is applicable to all heterogeneous systems. This rule was deduced on the basis of thermodynamic principles by J. Willard Gibbs . This rule predicts qualitatively the effect of temperature, pressure and concentration on a heterogeneous equilibrium.

# Phase Rule

## Gibbs phase rule may be stated as follows:

When the equilibrium between any numbers of phases is influenced only by temperature, pressure and concentration but not influenced by gravity, electrical and magnetic forces, then the number of degree of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the Phase Rule equation:

$$F = C - P + 2$$

where

F = number of degree of freedom

C = number of components

P = number of phases

2 = variables depending on temperature and pressure besides the concentration variables.

# Phase Rule

## Phase Rule :

Gibbs phase rule may be also mathematically stated as follows :

"In a heterogeneous system in equilibrium, the number of degrees of freedom plus the number of phases is equal to the number of components plus two".

$$\text{Mathematically, } F + P = C + 2$$

$$\text{or } F = C - P + 2$$

where

F = number of degrees of freedom

C = number of components

P = number of phases

2 = variables depending on temperature and pressure besides the concentration variables.

# Phase Rule

**Phase:** The chemically homogeneous, physically distinct and mechanically separable part of a system which is separated by a definite boundary from other such parts of the system is called phase". It is denoted by P.

## Examples

- (i) A gaseous mixture constitutes a single phase since gases are completely miscible. Air is a mixture of  $N_2$ ,  $O_2$ ,  $CO_2$ , water vapour etc. Which constitute a single phase.
- (ii) Two or more liquids which are miscible with one another constitute a single phase as there is no bounding surfaces separating the different liquids. e.g., water and alcohol, benzene & chloroform constitute one phase system.
- (iii) A system consisting of a liquid in equilibrium with its vapour constitute a two phase system
- (iv) Solid  $\rightleftharpoons$  Liquid  $\rightleftharpoons$  Vapour  $P = 3$
- (v)  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$   $P = 3$
- (vi) Water - phenol  $P = 2$



# Phase Rule

## Component :

The number of component of a system at equilibrium is defined as the minimum number of independently variable constituents which are required to express the composition of each phase in the system. It is denoted by C.

In a chemically reactive system, the number of components is given by

$$C = N - E$$

where C = components.

N = Number of chemical species

E = Number of independent equations relating the concentrations of the N species.

- If you have equilibrium balance between reactants and products, the number of components will be reduced by one
- If you have equal amounts (concentrations) of products formed, the number of components will also be reduced by one

# Phase Rule

## Examples

- (i) **Sulphur system:** Consists of four phases namely monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphur vapour. The composition of each phase of the system can be expressed in terms of sulphur only, so, it is a one component system.  $C = 1$

Rhombic sulphur - Monoclinic sulphur – Sulphur liquid – Sulphur vapour

- (ii).  **$\text{Na}_2\text{SO}_4$  + water system:** Certain salts are capable of existing as hydrates with different number of water molecules of crystallization. These hydrates correspond to different solids and hence to different phases. The system is a two component, because the composition of each phase of the hydrates is completely described in terms of the anhydrous salt and water alone.  
e.g.,  $\text{Na}_2\text{SO}_4$  + water  $C = 2$

- (iii). **Water  $\rightleftharpoons$  Ice  $\rightleftharpoons$  Water vapour**  $C = 1$

- (iv) **KCl - NaCl –  $\text{H}_2\text{O}$  system**

$$C = N - E = 3 - 1 = 2$$

- (v) **KCl – NaBr –  $\text{H}_2\text{O}$  system**

$$N = 5, \quad E = 1$$

$$C = 5 - 1 = 4$$

- (vi)  **$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$**

$$C = N - E = 3 - 1 = 2$$

# Component

## Number of Components

- NaCl(s) dissolved in water
  - Available chemical constituents are four.  $\text{Na}^+$ ,  $\text{Cl}^-$ , NaCl and  $\text{H}_2\text{O}$
  - Because  $\text{Na}^+$  and  $\text{Cl}^-$  have the same amount “equal neutrality” as NaCl, then  $c = 2$  and not 4
- Decomposition of calcium carbonate
$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$
  - Available chemical constituents are three. Is it correct to say  $c = 3$  ?
  - Because of the equilibrium condition the number of independent components is reduced by one. Thus,  $c = 2$  instead of 3;  $C = 2$ ,  $P = 3 \rightarrow F = 2 - 3 + 2 = 1$
- Decomposition of ammonium chloride
$$\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$$
  - Available chemical constituents are three. Is it correct to say  $c = 3$  ?
  - Because of the equilibrium condition the number of independent components is reduced by one. And also because the products formed form a single phase and are formed in equal amounts, the no. of independent components are further reduced by one.
  - $C = 1$ ,  $P = 2 \rightarrow F = 1 - 2 + 2 = 1$
- Decomposition of  $\text{PCl}_5$ 
$$\text{PCl}_5(s) \rightleftharpoons \text{PCl}_3(s) + \text{Cl}_2(g)$$
  - Available chemical constituents are three. Is it correct to say  $c = 3$  ?
  - Because of the equilibrium condition the number of independent components is reduced by one.  $C = 2$ ,  $P = 3 \rightarrow F = 2 - 3 + 2 = 1$

# Phase Rule

## Degree of Freedom :

The degree of freedom or variance of a system is defined as the minimum number of variable factors such as temperature, pressure and concentration which should be required in order to define the system completely. It is denoted by  $F$ .

## Examples

- (i) For a given sample of any gas  $PV = nRT$ . Any two of the three variables  $P$ ,  $V$ ,  $T$  define the system completely. Hence the system is bivariant or it has two degrees of freedom.



# Phase Rule

## Conclusion-

- (i) The greater the number of components in a system, the greater is the degree of freedom for a given number of phases.
- (ii) The greater the number of phases, the smaller is the number of degrees of freedom.
- (iii) The number of phases is maximum when the number of degrees of freedom = Zero, for a given number of components. Thus, for
  - one component system,  $P_{\max.} = 3$  .
  - two component system,  $P_{\max.} = 4$
  - three component system,  $P_{\max.} = 5$

# Phase Rule

## **Advantages of Phase' Rule :**

- (i) The phase rule confirms that the different systems having the same number of degrees of freedom behave in same manner.

## **Limitations:**

- (i) The phase rule is applicable to heterogeneous systems in equilibrium, so, it is of no use for such systems which are slow in attaining the equilibrium state.
- (ii) In Gibbs phase rule, various variables are temperature, pressure and composition. It does not take in account the electric and magnetic influences. For consideration of such variables, the factor 2 of the Phase rule has to be adjusted accordingly.
- (iii) All the phases in the system must be present under the same temperature, pressure and gravitational force .

# Phase Rule

## Phase diagrams :

The number of phases that exist in equilibrium depends upon the conditions of temperature and pressure, composition being constant or temperature and composition, pressure being constant. These conditions are determined experimentally and interdependence of values of the variables can be shown graphically using appropriate coordinates. These diagrams are termed phase diagram. **A phase diagram is the description of the behaviour of the phases under equilibrium.** It is very easy to describe the phase behaviour of a system by such diagrams and to investigate the conditions in which various phases will constitute the system .

# Phase Rule

## Application of Gibbs Phase Rule to One Component System:

From the mathematical expression,

$$F = C - P + 2$$

For maximum value of degree of freedom ( $F_{\text{max.}}$ )

$$C = 1, P = 1$$

$$\begin{aligned} F_{\text{max.}} &= 1 - 1 + 2 \\ &= 2 \end{aligned}$$

Hence, all one component systems can be completely described graphically by stating only two variables, pressure and temperature on appropriate axis.

# Phase Rule

## The Water System :

It is a one component system. Water exists in three possible phases viz. ice (solid) , water (liquid), and vapour (gas). These three single phases may form four possible equilibria.

(i) Solid  $\rightleftharpoons$  Liquid

(ii) Liquid  $\rightleftharpoons$  Vapour

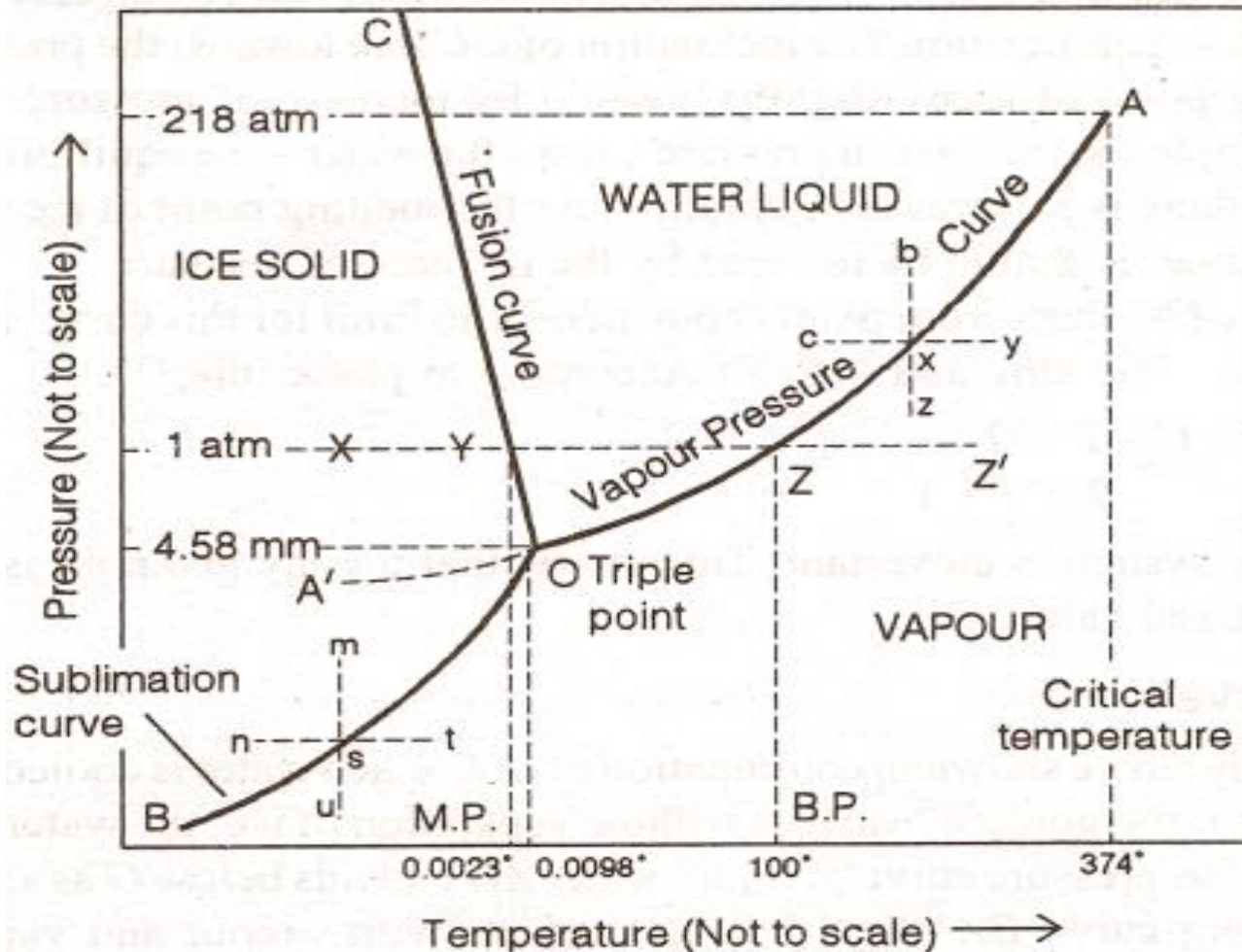
(iii) Solid  $\rightleftharpoons$  Vapour

(iv) Solid  $\rightleftharpoons$  Liquid  $\rightleftharpoons$  Vapour

The Phase diagram of water system is given as

# Phase Rule

## Phase Diagram of water system



# Phase Rule

The phase diagram consists of :

- (i) Stable curves: three  $OB$ ,  $OA$  and  $OC$
- (ii) Metastable curve: one  $OA'$
- (iii) Areas: three  $AOB$ ,  $COB$  and  $AOC$
- (iv) Triple point: One at  $O$
- (v) Critical point A: Critical temperature ( $374^{\circ}\text{C}$ ) and critical pressure ( $218 \text{ atm.}$ ). Above critical temp. only vapour phase exists whatever may be the value of pressure. The vapour pressure of water increases with increase in temperature. Above the critical temperature and critical pressure, liquid and vapour phase can not be distinguished and a **super critical fluid** is obtained.

## (i) Stable curves

**OA** : It is known as **vapour pressure curve of water**. The curve  $OA$  starts from point  $O$  i.e.,  $0.0098^{\circ}\text{C}$  under  $4.58 \text{ mm of Hg}$  pressure and ends at  $A$ , the critical point ( $374^{\circ}\text{C}$  at  $218 \text{ atm.}$ ).

# Phase Rule

The rate of increase of its vapour pressure with temperature is relatively higher at higher temperatures and therefore the curve OA slants upwards and slopes away from the temperature axis.



From phase rule,

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 2 + 2 \\ &= 1 \end{aligned}$$

The water vapour system is univariant



# Phase Rule

**OB** : It is the **sublimation curve of ice**. Along this curve, solid ice is in equilibrium with its vapour.

This curve is not the prolongation of curve A but falls off more steeply. At all points of the curve *OB*, ice is in equilibrium with vapour. Hence, there are two phases.

Solid  $\rightleftharpoons$  Vapour       $P = 2$

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$= 1$$

Thus, the system is univariant. This means that for each temperature; there may be one pressure and for each pressure there may be one temperature.

# Phase Rule

**OC** : This curve is the **melting point curve or fusion curve of ice**. Along this curve two phases, ice and water are in equilibrium. The inclination of OC line towards the pressure axis indicates that the melting point of ice is slightly lowered by increase of pressure. (According to Le Chatelier's principle the increase in pressure causes the water - ice equilibrium to shift in such a direction that there is a decrease in volume). As the melting point of ice is accompanied by decrease in volume, it should be lowered by the increase of pressure.



According to phase rule,

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 2 + 2 = 1 \end{aligned}$$

Thus, the system is univariant. This means that for any given pressure, melting point must have one fixed value.

# Phase Rule

## (ii) Metastable Curve

**OA'** : It is a metastable curve shown in continuation of *AO*. When water is cooled below its freezing point (when it is not vigorously stirred) without separation of ice, the water is said to be **super cooled**. The vapour pressure curve of liquid water *AO* extends below *O* as shown by the dotted curve *OA'*. Along curve *OA'* liquid water coexists with vapour and vapour pressures are different than over the solid. This equilibrium is called metastable equilibrium as slight disturbance brings it to the stable region *OB* of the phase diagram.

Liquid  $\rightleftharpoons$  Vapour       $P = 2$

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$= 1 \quad \text{Monovariant}$$

# Phase Rule

## (iii) Areas

The areas give the conditions of temperature and pressure under which single phase - ice (solid), water (liquid) and vapour(gas) can exist. It is necessary to specify both temperature and pressure to define a system within this area. In the area  $BOC$ ,  $AOC$  and  $AOB$  exists, ice (solid), water (liquid) and vapour (gas) respectively. In these areas, the degrees of freedom for the system is two or they are bivariant.  $P = 1$      $F = 2$

## (iv) The Triple point O

The point O at which the curves  $AO$ ,  $BO$  and  $CO$  meet is called the triple point. At this point all the three phases viz , ice, water and vapour co-exist. Thus,  $P = 3$ .



$$F = C - P + 2, \quad F = 1 - 3 + 2 \quad F = 0 \quad \text{Nonvariant}$$

# Phase Rule

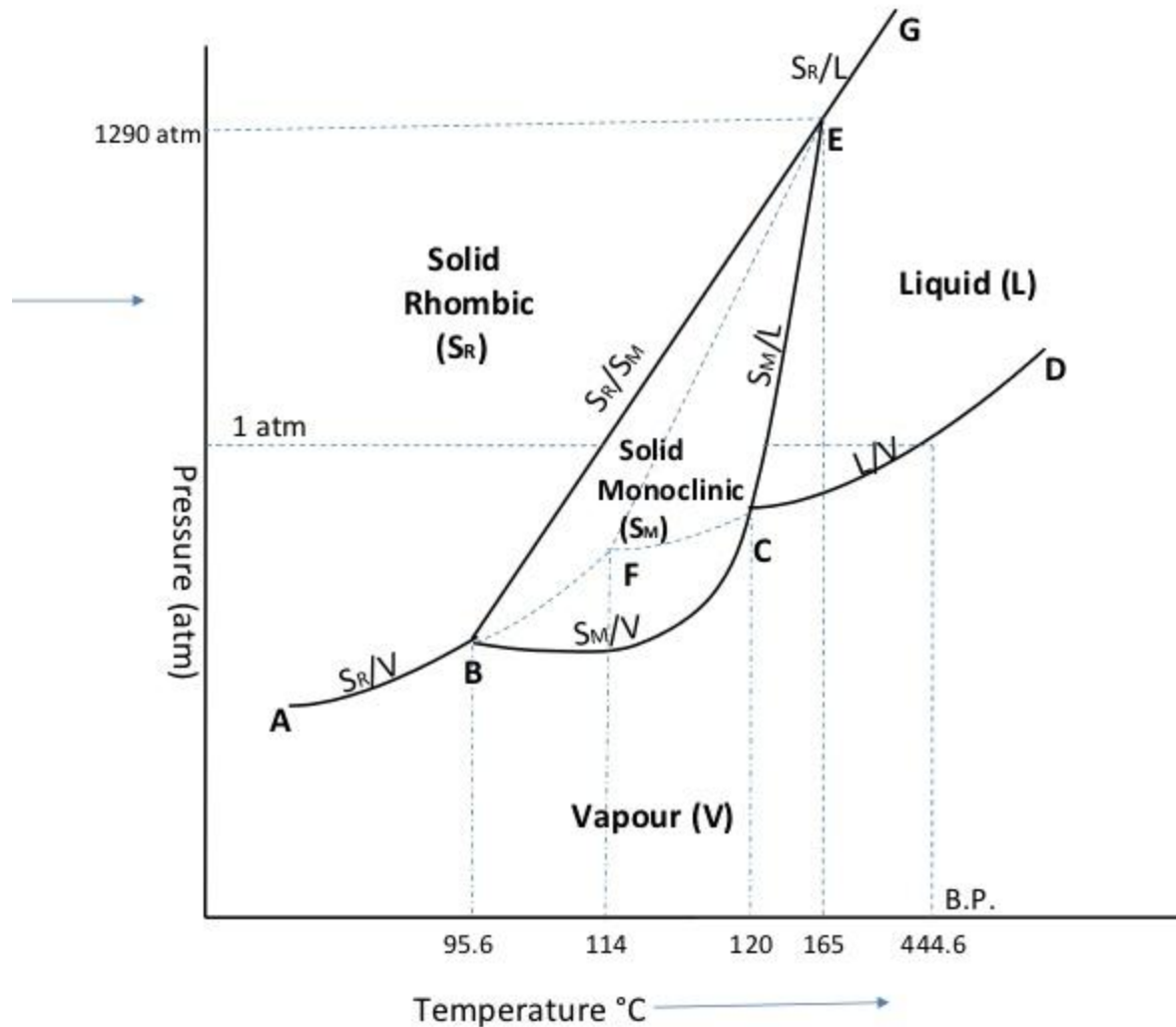
Thus, the degree of freedom at triple point is zero, which indicates that there is only one set of variables  $P$ ,  $T$  at which all the three phases coexist.

The triple point O is a self defined point corresponding to  $0.0098^{\circ}\text{C}$  temperature and 4.58 mm of Hg pressure.

**(v) Critical point A:** Critical temperature ( $374^{\circ}\text{C}$  ) and critical pressure (218 atm.). Above critical temp. only vapour phase exists whatever may be the value of pressure. The vapour pressure of water increases with increase in temperature. Above the critical temperature and critical pressure, liquid and vapour phase can not be distinguished and a **super critical fluid** is obtained.

## Phase Diagram of Sulphur

Sulphur exist in 4 phases Rhombic sulphur ( $S_R$ ), Monoclinic sulphur ( $S_M$ ), Sulphur liquid (L) and Sulphur vapour (V)



# Sulphur

From phase rule, if  $P = 4$   $F = C - P + 2 = 1 - 4 + 2 = -1$

Since degree of freedom may not be negative therefore all the four form of sulphur can not co-exist at any point of the phase diagram of sulphur.

- Curve AB is sublimation curve  $S_R \rightleftharpoons V$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve BC is sublimation curve  $S_M \rightleftharpoons V$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve CD is vapour pressure curve  $L \rightleftharpoons V$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve CE is fusion curve  $S_M \rightleftharpoons L$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve EG is fusion curve  $S_R \rightleftharpoons L$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve BE is transition curve  $S_R \rightleftharpoons S_M$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve BF is metastable curve  $S_R \rightleftharpoons S_V$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve CF is metastable curve  $L \rightleftharpoons V$   $F = 1 - 2 + 2 = 1$  monovariant
- Curve EF is metastable curve  $S_R \rightleftharpoons L$   $F = 1 - 2 + 2 = 1$  monovariant
- B is triple point  $S_R \rightleftharpoons V \rightleftharpoons S_M$   $F = 1 - 3 + 2 = 0$  nonvariant
- C is triple point  $S_M \rightleftharpoons V \rightleftharpoons L$   $F = 1 - 3 + 2 = 0$  nonvariant
- E is triple point  $S_R \rightleftharpoons L \rightleftharpoons S_M$   $F = 1 - 3 + 2 = 0$  nonvariant
- F is metastable triple point  $S_R \rightleftharpoons V \rightleftharpoons L$   $F = 1 - 3 + 2 = 0$  nonvariant
- Under the areas, ABG, DCG, DGBA and BCEB,  $P = 1$  and  $F = 2$

# POLYMORPHISM

- **POLYMORPHISM:** The occurrence of the same substance in more than one crystalline forms is known as Polymorphism. This phenomenon is shown by both elements and compounds. In the case of elements the term allotropy is often used. The individual crystalline forms of an element are referred to as polymorphs or allotropes. Rhombic and monoclinic sulphur are two polymorphs or allotropes of sulphur. The polymorphic or allotropic forms of an element have distinct physical properties and constitute separate phases.

Allotropy can be divided into three types : Enantiotropy, Monotropy and Dynamic allotropy.

- **Enantiotropy:** In some cases one polymorphic form (or allotrope) can change into another at a definite temperature when the two forms have a common vapour pressure. This temperature is known as the transition temperature. One form is stable above this temperature and the other form below it. When the change of one form to the other at the transition temperature is reversible, the phenomenon is called enantiotropy and the polymorphic forms enantiotropes. For example, rhombic sulphur on heating changes to monoclinic sulphur at 95.6° C (transition temperature). Also, monoclinic sulphur, on cooling, again changes to rhombic sulphur at 95.6°C. That is, 95.6°C

Rhombic sulphur  $\rightleftharpoons$  Monoclinic sulphur

Thus Rhombic sulphur and Monoclinic sulphur are enantiotropic.



## POLYMORPHISM:

- **Monotropy:** It occurs when one form is stable and the other metastable. The metastable changes to the stable form at all temperatures and the change is not reversible. Thus there is no transition temperature as the vapour pressures are never equal. This type of polymorphism is exhibited by phosphorus, White phosphorus  $\longrightarrow$  Red phosphorus. Another example is graphite and diamond, graphite being stable and diamond metastable, although the change is infinitely slow.
- **Dynamic allotropy:** Some substances have several forms which can coexist in equilibrium over a range of temperature. The amount of each is determined by the temperature. The separate forms usually have different molecular formulae but the same empirical formula. This form of allotropy, known as dynamic allotropy, resembles enantiotropy in that it is reversible but there is no fixed transition point. An example of dynamic allotropy is provided by liquid sulphur which consists of three allotropes  $S_\mu$ ,  $S_\pi$  and  $S_\lambda$ .  $S_\mu \rightleftharpoons S_\pi \rightleftharpoons S_\lambda$  These three forms of sulphur differ in molecular structure.  $S_\lambda$  is  $S_8$ ,  $S_\pi$  is  $S_4$  while formula of  $S_\mu$  is not known. The composition of the equilibrium mixture at 120°C and 444.6°C (b.p. of sulphur) is :
  - 120°C  $S_\mu$  0%  $S_\pi$  3.7%  $S_\lambda$  96.3%
  - 444.6°C  $S_\mu$  37%  $S_\pi$  4%  $S_\lambda$  59%

## Clapeyron – Clausius equation

The variation of vapour pressure with temperature is quantitatively given by Clapeyron – Clausius equation as follows

$$\frac{dP}{dT} = \frac{\Delta H_v}{T (V_g - V_l)}$$
$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

Where  $V_l$  = Molar volume of liquid water,  $V_g$  = Molar volume of liquid vapour or steam,  $\Delta H_v$  = Heat of vaporization

The variation of sublimation of ice with temperature is quantitatively given by Clapeyron – Clausius equation as follows

$$\frac{dP}{dT} = \frac{\Delta H_s}{T (V_g - V_s)}$$
$$\ln \frac{P_2}{P_1} = \frac{\Delta H_s}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

Where  $V_s$  = Molar volume of ice,  $V_g$  = Molar volume of liquid vapour or steam,  $\Delta H_s$  = Molar heat of sublimation of ice

The variation of fusion of ice with temperature is quantitatively given by Clapeyron – Clausius equation as follows

$$\frac{dP}{dT} = \frac{\Delta H_f}{T (V_l - V_s)}$$

Where  $V_s$  = Molar volume of ice,  $V_l$  = Molar volume of water,  $\Delta H_f$  = Molar heat of fusion of ice

# Two component system

For two component system

$$C = 2$$

For maximum number of degree of freedom  $P = 1$

$$\text{Therefore } F_{\max.} = 2 - 1 + 2 = 3$$

Thus, the variables (T, P, and composition) are required to define the system completely. But three variables can not be plotted in 2D figures (phase diagram). Therefore one of the degree of freedom is reduced by taking it as constant. Now we have taken P constant. Then

$F = C - P + 2$  becomes

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

**$F = C - P + 1$**  which is known as reduced phase rule equation. The reduced phase rule equation is used for calculation of degree of freedom for two component systems.

# Phase diagram of two component Liquid – Liquid system

## Water – phenol system

- Water and phenol are partially miscible to each other. Therefore when we take water and phenol together, we get two phases, one is saturated solution phenol in water and other is saturated solution of water in phenol. The solution containing these two phases having different composition in equilibrium, are called **conjugate solution**. The mutual solubility of these two phases increases by increasing the temperature or decreasing the temperature and reach at a temperature where both the phases becomes completely miscible and two phase system is converted to one phase system. This temperature is known as **critical solution temperature (CST)**. If two phase system is converted to one phase system by increasing the temperature, it is known as upper critical solution temperature (**UCST**). If two phase system is converted to one phase system by decreasing the temperature, it is known as lower critical solution temperature (**LCST**).

# Liquid – Liquid System



## SOLUBILITY OF LIQUIDS IN LIQUIDS

There are liquids:

- ❖ Showing complete miscibility e.g. water & ethyl alcohol
- ❖ Showing complete immiscibility e.g. water & mercury
- ❖ Showing partial miscibility e.g. water & phenol

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## In cases of partial miscibility

Degree of miscibility may be dependent on the temperature

1. Solubility ↑ with ↑ in temperature (water-phenol)
2. Solubility ↓ with ↑ in temperature (water-triethylamine)
3. Solubility ↑ with ↓ & ↑ in temperature (water-nicotine)
4. Solubility not affected by temperature

In case of three component system the third liquid may influence the degree of solubility of the 2 liquid systems.

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# Liquid – Liquid System



**Effect of temperature variation on the degree of miscibility in these systems is described by means of phase diagrams.**

## **Phase diagrams**

= graphs of temperature versus composition at constant P



## **1. Systems showing an increase in miscibility with rise in temperature**

❖ A +ve deviation from Raoult's law due to difference in the cohesive forces that exist between the molecules of each component in a liquid mixture.



❖ Each phase consists of a saturated solution of one component in the other liquid.

❖ Such saturated solutions are known as **conjugate solutions**



# Liquid – Liquid System



## Phenol and water system phase diagram.

**Temperature fixed at 50 °C**

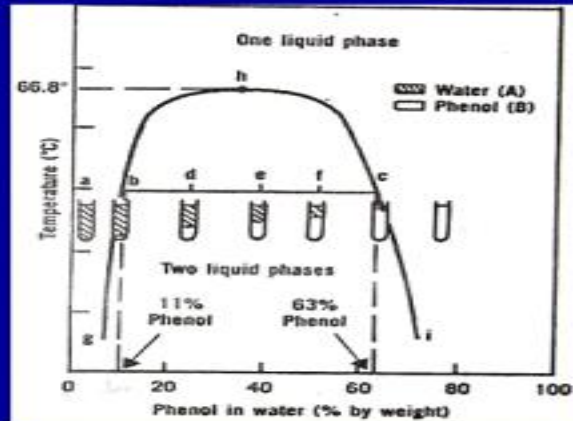
- \* Point **a**, system containing 100% pure water.

Addition of phenol to water will result in the formation of a single liquid phase until the point **b** is reached.

- \* At point **b**, appears a second phase.

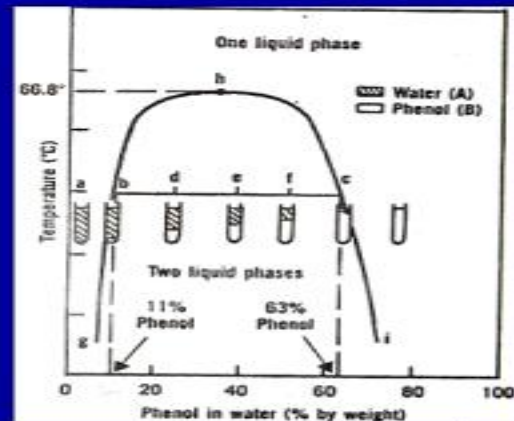
**Phase A:** water rich phase containing 11% phenol

**Phase B:** phenol rich phase containing 63% phenol



\* increasing quantities of phenol, i.e., as we proceed across the diagram from point **b** to point **c**, we form systems in which the amount of the phenol-rich phase (B) continually increases

- \* At the same time the amount of the water-rich phase (A) decreases. Once the total conc. of phenol exceeds 63 % at 50 °C a single phenol-rich liquid phase is formed.



# Liquid – Liquid System



**At 50°C**

**Aqueous phase saturated with phenol:**

contains **11%** phenol (point b)

**Phenolic phase saturated with water:**

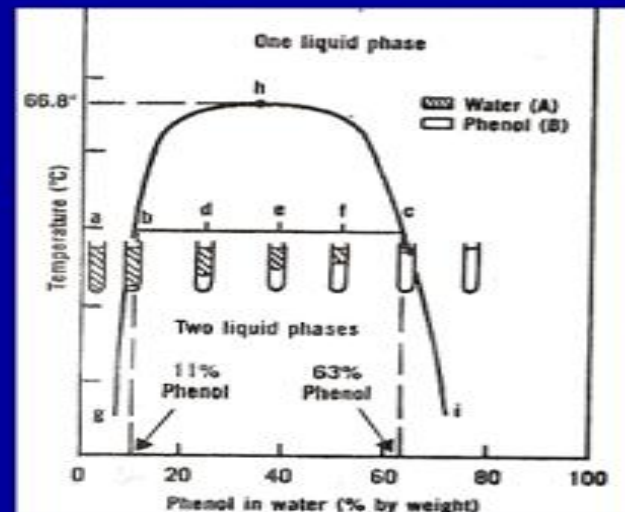
contains **63%** phenol (point c)

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\* The **line bc** drawn across the region containing two phases is termed a **tie line**; it is always parallel to the base line in two component systems.

\* all systems prepared on a tie line at 50° C will separate into phases of constant composition whose composition is **b** and **c**. These phases are termed **conjugate phases**.



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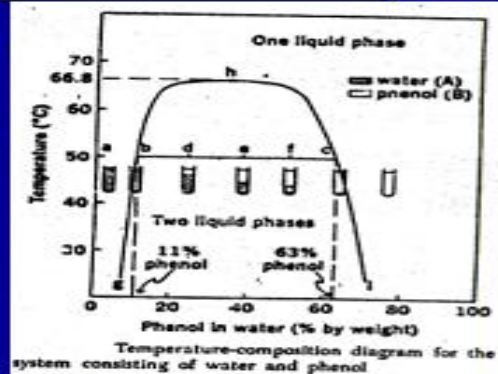


# Liquid – Liquid System

*The critical solution temperature  
(upper consolute temperature):*

Is the maximum temperature at which the two phase region exists. In the case of the phenol-water system this is 66.8° (point *h* in Figure).

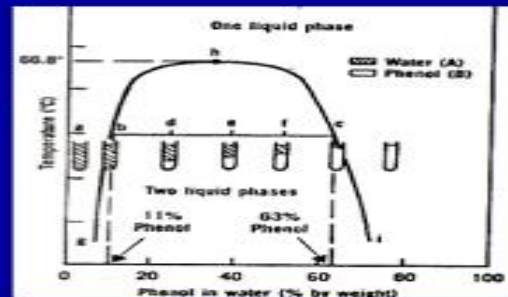
✎ All combinations of phenol and water above this temperature are completely miscible and yield one-phase liquid systems.



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✳ All combinations of phenol and water above this temperature are completely miscible and yield one-phase liquid systems.



# Liquid – Liquid System



## 2. Systems showing a decrease in miscibility with rise in temperature

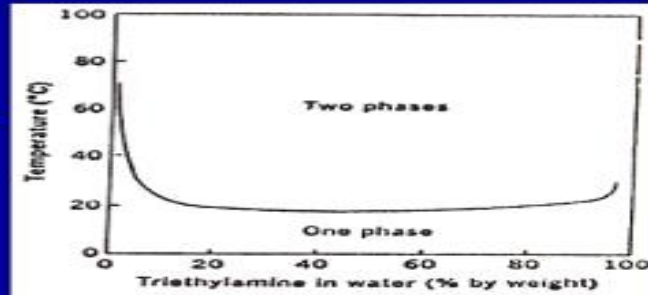
### TRIETHYLAMINE & WATER

The solubility of liquid pairs may increase as the temperature is lowered

The system will exhibit a *lower consolute temp.*

Below which the two members are soluble in all proportions

Above which two separate layers are formed.

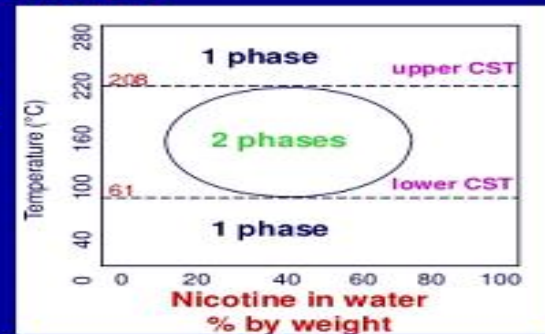


## 3. Systems showing upper and lower consolute temperature

### NICOTINE & WATER

Mixtures such as nicotine & water show both an **upper** and **a lower consolute temperature**

with an intermediate temperature region in which the two liquids are only partially miscible.



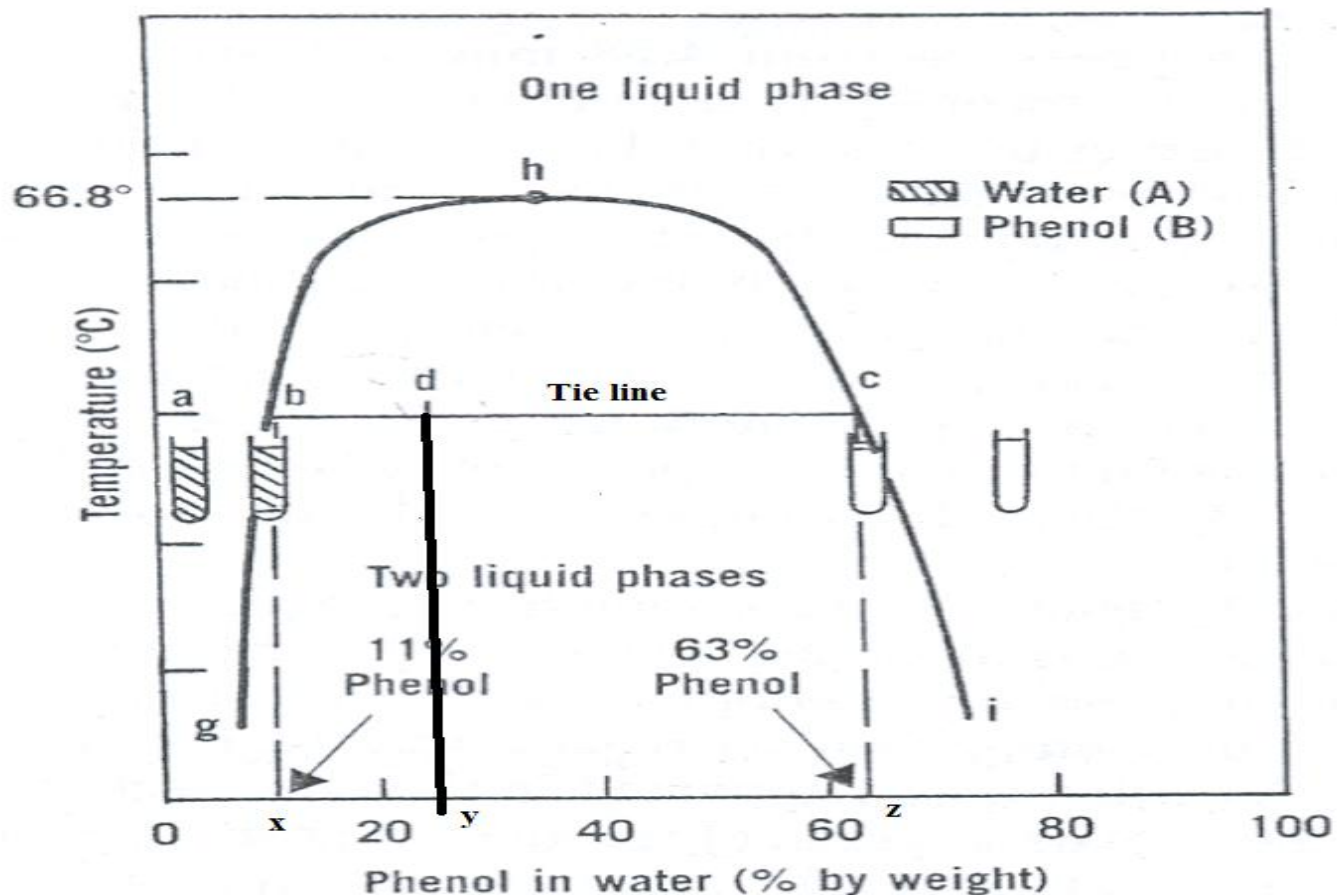
## 4. Systems with no critical solution temperature

The pair, **ethyl ether and water**, has neither an upper nor a lower consolute temperature and shows partial miscibility<sup>15</sup> over the entire temperature range at which the mixture exists.

**Lever Rule :** It is used to determine the ratio of the amount of the two phases at a particular point inside the phase diagram

$$m_1 / m_2 = dc/db = (z - y) / (y - x)$$

$m_1$  is amount of phase b and  $m_2$  is amount of phase c





# Liquid – Liquid System



## The effects of added substances on critical solution temperatures

Critical solution temperatures are very sensitive to impurities or added substances.

The addition of a substance to a binary liquid system produces a ternary system.

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The effects of additives on CST

Type of CST	Solubility of additive in each component	Effect on CST	Effect on miscibility
Upper	Approx. equally soluble in both components	Lowered	Increased
Upper	Readily soluble in one component but not in other	Raised	Decreased
Lower	Approx. equally soluble in both components	Raised	Increased
Lower	Readily soluble in one component but not in other	Lowered	Decreased



A) If the added material is soluble in only 1 of the 2 components or if the solubility in the two liquids are markedly different, the solubility of the liquid pair is **decreased** due to **salting-out**

If the original binary mixture has an upper CST, the T  $\uparrow$  if it has a lower CST, the T  $\downarrow$  by the addition of the third component.

### Example:

If 0.1 M naphthalene is added to a mix. of phenol and water it dissolves only in the phenol and raises the CST about 20°;

If 0.1 M KCl is added to a phenol-water mix, it dissolves only in water and raises the CST approximately 8°.

# Liquid – Liquid System



**B)**

If the added material is soluble in both of the liquids to about the same extent, the solubility of the liquid pair is increased;

The increase in solubility of two partially miscible solvents by an additive is referred to as *blending*.  
an upper CST is lowered and a lower CST is raised.

*Example:*

The addition of succinic acid or Na oleate to a phenol-water system.

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*Example:*

A mixture of phenol and water at 20° C has a total composition of 50 % phenol. The tie line at this temperature cuts the curve at points equivalent to 8.4 and 72.2 per cent w/w phenol.

- What is the weight of the aqueous layer and of the phenol layer in 500 g of the mixture?
- How many g of phenol are present in each of the two layers?

*Solution:*

Let Z be the weight in grams of the aqueous layer.

(500 - Z) is the weight in grams of the phenol layer.

The sum of the percentages of phenol in the two layers =

$$500 \times 50/100 = 250 \text{ g}$$

$$Z (8.4/100) + (500 - Z)(72.2/100) = 250$$

$$1) \text{ weight of aqueous layer } Z = 174 \text{ g}$$

$$\text{weight of phenol layer } (500 - Z) = 326 \text{ g}$$

$$2) \text{ The weight of phenol in the aqueous layer}$$

$$174 \times 8.4/100 = 15 \text{ grams}$$

$$\text{The weight of phenol in the phenolic layer}$$

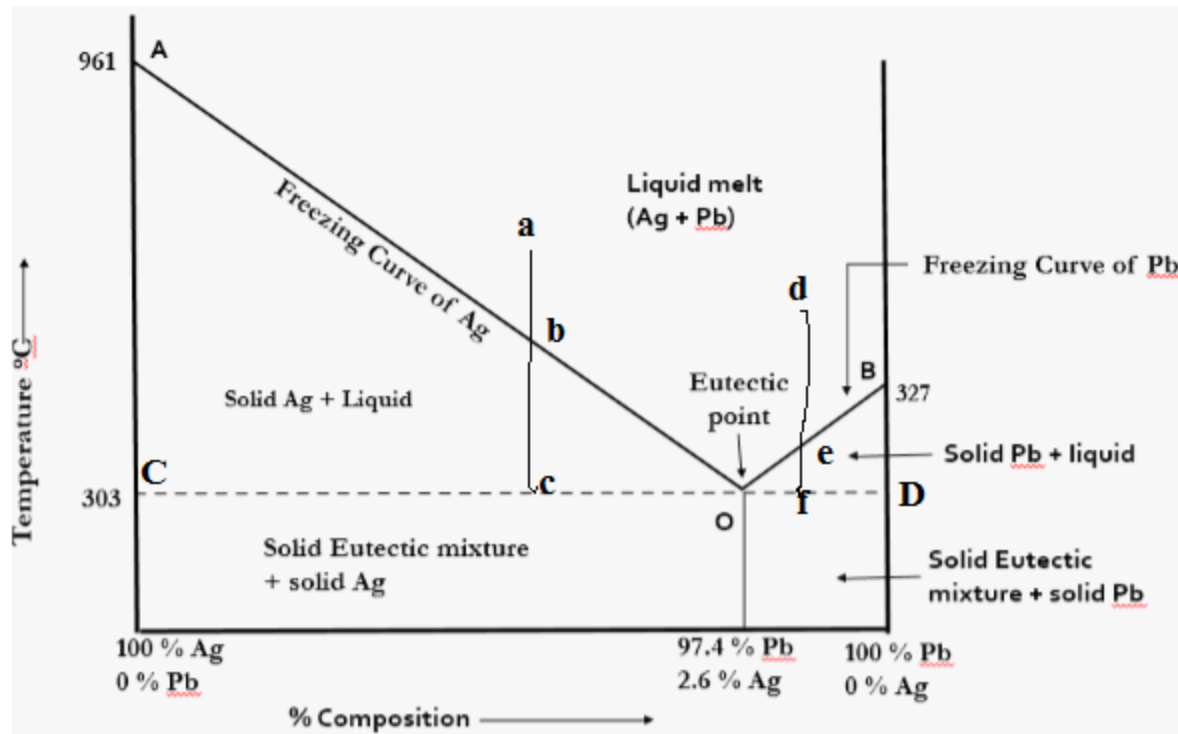
$$326 \times 72.2/100 = 235 \text{ grams}$$



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# Two component Solid – Liquid system

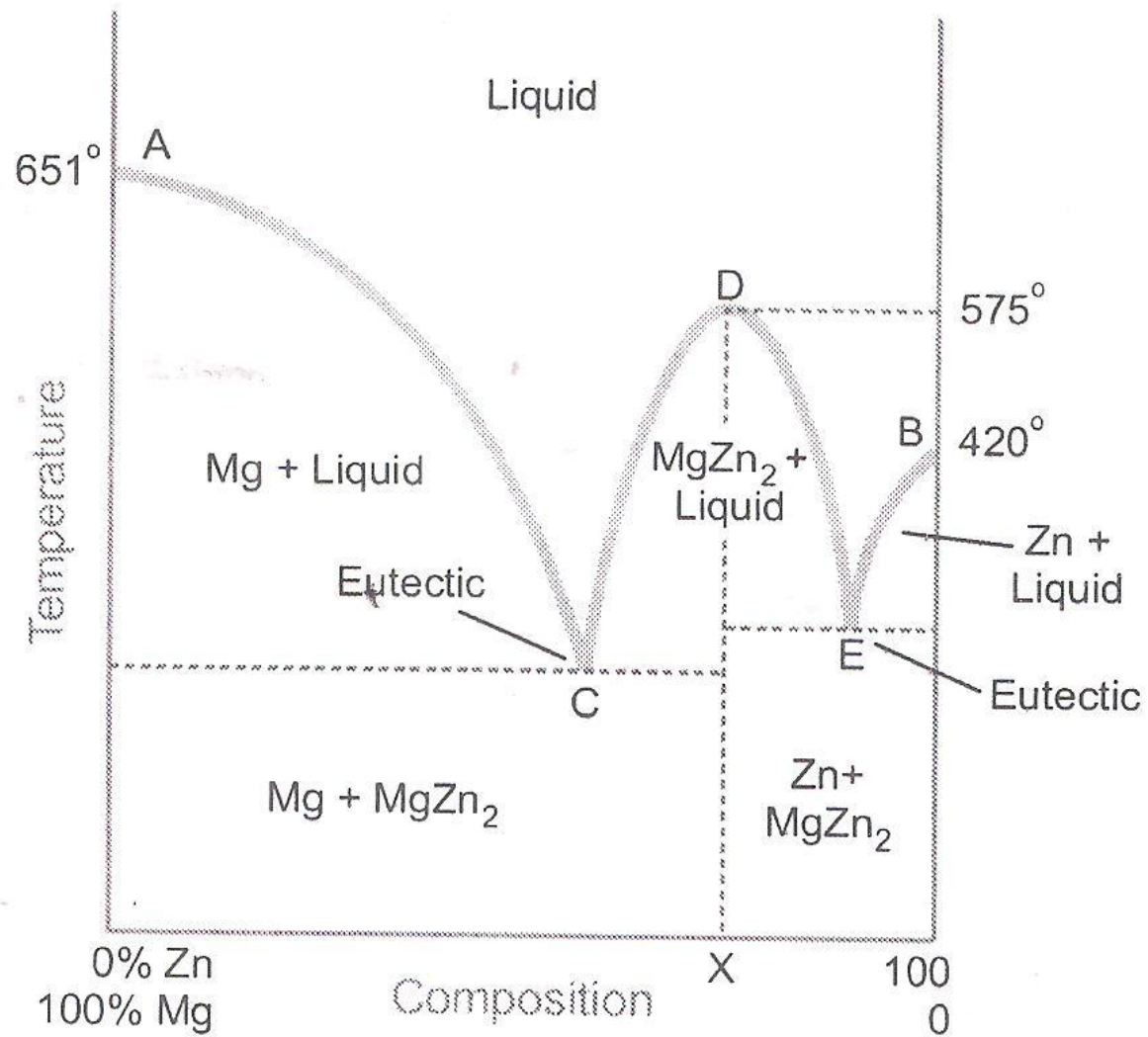
- Eutectic Mixture : If both the components are completely miscible in liquid (molten) state, immiscible in solid state and do not react with each other then combination of both form eutectic mixture. Example: Pb- Ag system.
- Phase diagram of Pb – Ag system



# Phase diagram of Pb – Ag system

- **Curve AO.** It is a freezing point curve of Ag. Solid Ag and liquid co-exists.  $P = 2$   
 $F = C - P + 1 = 2 - 2 + 1 = 1$   
Therefore, system is univariant
  - **Curve BO.** It is a freezing point curve of Pb. Solid Pb and liquid co-exists.  $P = 2$   
 $F = C - P + 1 = 2 - 2 + 1 = 1$   
Therefore, system is univariant
  - **Point O.** It is eutectic point. Here 3 phases (solid Ag, solid Pb and liquid) co-exists  
Eutectic temperature is the lowest temperature at which the liquid melt can exist.  $P = 3$   
 $F = C - P + 1 = 2 - 3 + 1 = 0$   
Therefore, system is nonvariant and temperature = 303 °C, Ag = 2.6 %
- Area AOB.** It represents solution of Pb Ag.  $P = 1$   $F = 2 - 1 + 1 = 2$  bivariant
- **Area ACO :** In area ACO Solid lead and melt are in equilibrium.  $P = 2$   $F = 1$
  - **Area BDO:** In area ACO Solid Ag and melt are in equilibrium.  $P = 2$   $F = 1$
  - **Area below line COD:** No liquid phase is present below line COD. Solid silver and solid lead are present in this area as two different phases.
  - $F = C - P + 1 = 2 - 2 + 1 = 1$ , monovariant
  - Application: Used in Pattison's process of desilverisation of Pb.
  - To increase % Ag in Argentiferous lead (0.1 % Ag) up to 2.6% Ag

## Phase Diagram of Zn – Mg System





## Phase Diagram of Zn – Mg System

- Systems in which two components form a solid compound.



The system will involve three solid phases, A, B and C. The fourth phase will be a liquid (or solution) containing varying concentration of A and B. There will be three freezing point or melting point curves.

- **The curve AC, CDE and BE:** AC is the freezing point curve of magnesium; BE is the freezing point curve of zinc; and CDE is that of the compound  $\text{MgZn}_2$ .
- The curve AC shows that the melting point of magnesium ( $651^\circ\text{C}$ ) is lowered on the addition of zinc. This continues until the point C is reached. Here a new phase, solid  $\text{MgZn}_2$  appears. The curve CD shows the increase of concentration of zinc in the melt with the rise of temperature. At the maximum point D, the composition of the melt and the solid compound becomes the same i.e.,  $\text{MgZn}_2$ . The point D, therefore, represents the congruent melting point of  $\text{MgZn}_2$  ( $575^\circ\text{C}$ ). The curve DE now shows the lowering of the melting point with the addition of zinc until the lowest point is attained. Here solid zinc appears. The curve BE exhibits that the melting point of zinc ( $420^\circ\text{C}$ ) falls with the addition of magnesium until the point E is reached. Along the freezing point curves AC, CDE and BE, there are two phases in equilibrium viz., one solid phase (Mg, Zn, or  $\text{MgZn}_2$ ) and the other liquid phase. Applying the reduced phase rule equation, we have

$F = C - P + 1 = 2 - 2 + 1 = 1$  This shows that the system Mg/liquid, Zn/liquid and  $\text{MgZn}_2$ /liquid are all monovariant.

## Phase Diagram of Zn – Mg System

- **Eutectic points C and E.** There are two eutectic points in the phase diagram. The systems at the points C and E have two components and three phases in equilibrium.
- Phases Present
- C Solid Mg, solid  $\text{MgZn}_2$ , Liquid
- E Solid Zn, solid  $\text{MgZn}_2$ , Liquid
- These systems are, therefore, nonvariant.  $F = C - P + 1 = 2 - 3 + 1 = 0$
- **Congruent Melting Point.** As already stated, the composition of the compound  $\text{MgZn}_2$  and the melt at D is identical. The corresponding temperature is the congruent melting point of the compound. Here the system has two phases viz., the solid compound and the melt. Both these can be represented by one component ( $\text{MgZn}_2$ ). Therefore the system at D is nonvariant,
- $F = C - P + 1 = 1 - 2 + 1 = 0$
- **The Areas.** The area above the curves AC, CDE and BE represents the solution of magnesium and zinc (the melt). The single phase system at any point in this area is bivariant.
- $F = C - P + 1 = 2 - 1 + 1 = 2$