

# PHASE RULE

## Gibb's Phase Rule

It states that in every heterogeneous system in equilibrium, the sum of the number of phases & degree of freedom is greater than the number

- $P + F = C + 2$
- Or
- $F = C - P + 2$
- Where,
- $P = \text{No. of phases}$
- $C = \text{No. of components}$
- $F = \text{No. of degrees of freedom}$

- This rule is valid for any system at equilibrium at definite temperature & pressure provided the equlibrium between any number of phases is not influenced by gravity, by electrical or magnetic forces.

## Phase

Phase is defined as any homogeneous , physically distinct, mechanically separable portion of the system which is separated from other parts of the system by definite boundary surfaces.E.g

Two immiscible liquids ( water & oil) (P=2)

Mixture of three solids  $\text{CaCO}_3$ ,  $\text{CuSO}_4$ ,  
 $\text{CaO}$

(P=3)



# Component

- The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed, either directly or in the form of chemical equation. E.g
- Ice (S)  $\leftrightarrow$  water(l)  $\leftrightarrow$  water vapour(g) ( C=1)
- $\text{CaCO}_3$  (S)  $\leftrightarrow$   $\text{CaO}(\text{S}) + \text{CO}_2$  (g) (C=2)
- As composition of each phase can be expressed in terms of at least any two of the constituents  $\text{CaCO}_3$ ,  $\text{CaO}$  &  $\text{CO}_2$
-

# Degree of freedom

- Degree of freedom is the minimum number of independently variable factors, such as temperature, pressure & composition of the phases, which must be arbitrarily specified in order to describe the state of the system completely. E.g
- In case of water system,
- Ice (S)  $\leftrightarrow$ water(l)  $\leftrightarrow$  water vapour(g) ( $F=0$ ) Triple point conditions.
- Water  $\leftrightarrow$  water vapour ( $F=1$ ) as only temp/ pressure to be specified to describe the system
- Completely)
- For gaseous system,  $PV = nRT$  hence ( $F= 2$ )

It is clear that for any one component-system the maximum number of degrees of freedom is two. Therefore, such a system can be represented completely by a two-dimensional diagram.

On the basis of experimental data obtained for the water system, a plot of relationships between the various phases (ice, water and vapour) under different conditions of temperature and pressure. (Temperature on x-axis and pressure on y-axis) drawn and resulting phase diagram is shown in Fig 4.1.

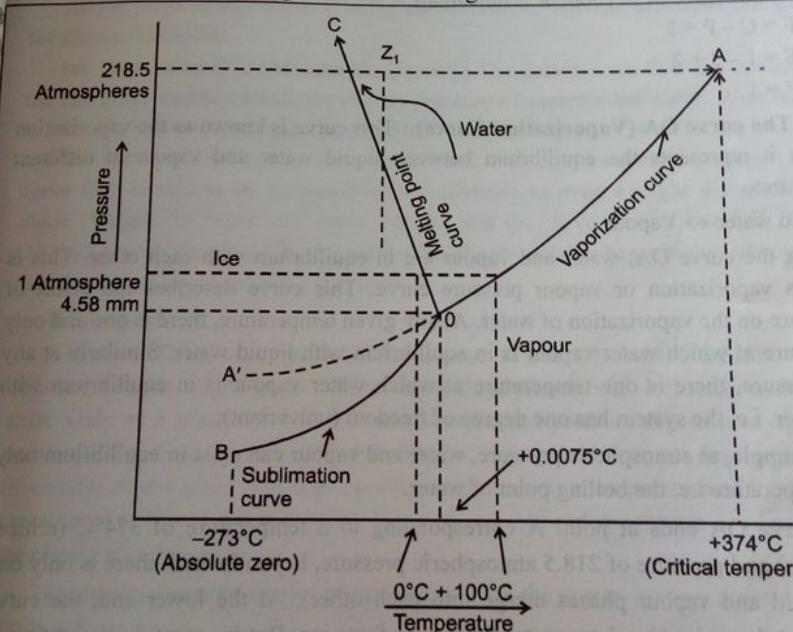


Fig. 4.1 : The Phase Diagram of Water System

#### (A) Area :

As can be seen from the diagram, there are three areas namely BOC (ice) and AOB (vapour). In any area, only one of the phases is present. To determine completely at any point in an area, both temperature and pressure should be known. The system in an area has two degrees of freedom (bivariant). The same can be shown by substituting the values of  $C = 1$  and  $P = 1$  in the phase rule equation

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

# Explanation of phase diagram of water

- $F = C-P+2$  for water system ( $C=1$ )
- $F= 1-P+2 = 3-P$
- The maximum value of  $F=2$  hence the phase diagram can be drawn by using two variables hence pressure & temperature are used for phase diagram.
- In the phase diagram, plot of relationship between the various phases (ice, water & vapour ) under different conditions of temperature & pressure ( temp on X-axis & pressure on Y-axis).

- **(A) Area**
- As can be seen from the diagram, there are three areas namely BOC (Ice), COA(water) & AOB (vapour). In any area, only one of the phases is present. To define the system completely at any point in an area, both temperature & pressure should be specified.
- So the system in area has two degrees of freedom ( system is bivariant). Same conclusion can be drawn by calculating F value.
- $F = C - P + 2 = 1 - 1 + 2 = 2$

- **Curve OA ( Vaporization Curve)**
- It represents the equilibrium between water & vapour at different temperature. At any given temperature , there is only one & one pressure at which water vapour is in equilibrium with water. Similarly at any given pressure , there is one temperature at which water vapour is in equilibrium with water. The curve OA ends at point A at a temp of  $374^{\circ}\text{C}$  (critical temperature) & critical pressure 218.5 atm. Beyond which liquid & vapour phases merge water behaves as fluid( supercritical fluid)

- $F=C-P+2$
- $= 1-2+2= 1$
- Hence at any given temperature , there is only one pressure at which water vapour is in equlibrium with water.
- Dotted curve OA' represent vapour pressure of super cooled water ( metastable phase). The vapour pressure of the meta stable phase is higher than that of stable phase.

- **Curve OB ( sublimation curve)**
- Along the curve OB, ice & vapour are in equilibrium with each other. The curve terminates at the lower end at absolute zero
- (-273<sup>0</sup>C) where no vapour can be present & only ice exists.
- $F = C - P + 2$
- $= 1 - 2 + 2$
- $= 1$
- Hence only one variable either P or T has to be specified to define the system completely.

- **Curve OC( Melting point curve)**
- Along this curve , two phases ice & water are in equilibrium with each other. This curve describes the effect of pressure on the melting point of the ice. The slope of the curve shows that
  - a) Increase of pressure decreases the melting point of the ice.
  - b) Ice melts with decrease in volume.
- $F= C-P+2= 1-2+2= 1$
- Hence only one variable P or T is to be specified to describe the system completely.

- **Triple Point:**
- Curves OA, OB & OC meet at point 'O' .
- This is called **triple point** where all the three phases ice, water & vapour co-exist.
- Only at a particular value of temperature (0.0075°C ) & a pressure of 4.58 mm. At this point , if we change either temperature or pressure , one of the phases will disappear.
- $F = C - P + 2$
- $= 1 - 3 + 2$
- $= 0$
- **Hence the system is non-variant.**

# Condense (Reduced) phase rule

In some systems, an equilibrium exists between solid - liquid phases and gaseous phase is practically absent. Hence the effect of pressure on such system can be neglected. Then it is necessary to take into account only two variables viz. temperature and concentration.

Such system showing solid-liquid equilibrium is called condensed system and phase rule applied to such systems is as follows:

$$F = C - P + 1 \dots \text{known as condensed phase rule.}$$

In the alloy system(Pb-Ag), Maximum degrees of freedom can be

$$F = C - P + 2$$

$$= 2 - P + 2 = 4 - P$$

Maximum degrees of freedom can be 3 . Since vapour phase is practically absent for alloy system, effect of pressure is negligible. Hence degrees of freedom considered here will be temperature & composition. As one degree of freedom is reduced here, modified phase rule will be

$$F = C - P + 1$$

which is also called as reduced phase rule

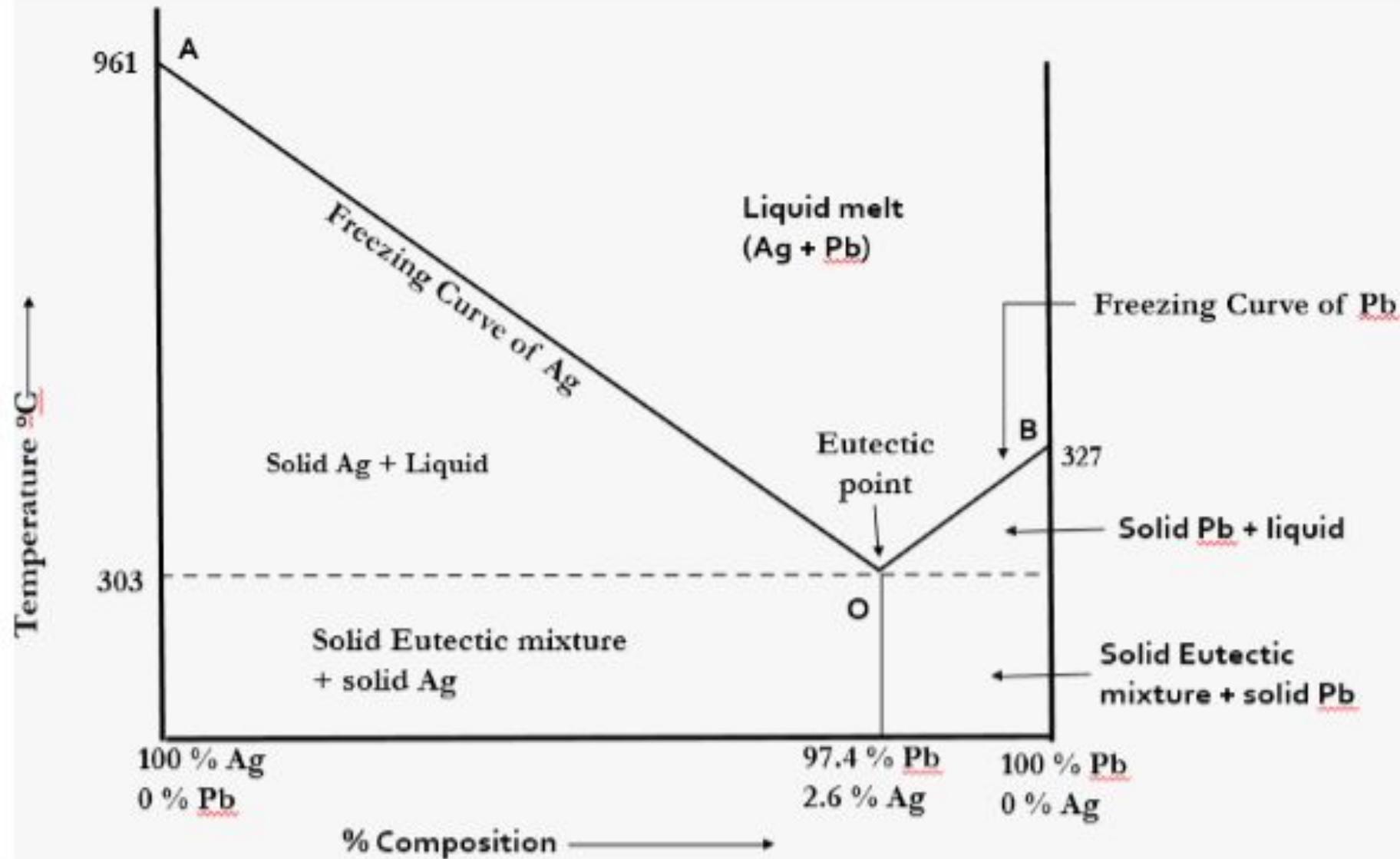
# Eutectic system

A binary system consisting of two substances , which are miscible in all proportions in liquid phase but which don't react chemically is known as the ‘Eutectic system’.

**Eutectic Mixture** : is a ‘solid solution’ of two or more substances having the lowest freezing point (melting point ) of all the possible mixtures of the components. This is taken advantage of in ‘ alloy of low melting points like solder , woods metal etc.

**Eutectic point** : is the lowest melting point attainable by eutectic mixture.

# Phase diagram of two component system(Pb-Ag alloy)



Pb-Ag alloy is two component system with four possible phases

solid Ag

solid Pb

Liquid (Pb+Ag)

vapour

In this vapour phase is practically absent as preparation of alloy is done at atmospheric pressure.

## Curve AO( freezing point curve of Ag)

shows the effect on freezing point of Ag on addition of lead (Pb) . The curve starts from A( $961^{\circ}\text{C}$ ), the melting point of Ag, where pure Ag exists as solid & liquid.

The curve indicates that the melting point of Ag falls gradually on adding Pb, along AO till the lowest point O( $303^{\circ}\text{C}$ ) is reached, where the solution gets saturated with respect to lead.

At O, no more lead can go in solution & consequently , melting point of Ag does not fall further .If any lead is added, it separates as the solid phase.

Along this curve solid Ag & Liquid(Ag+Pb) coexist

$$F = C - P + 1 = 2 - 2 + 1 = 1 \text{ ( system is Univariant)}$$

The point ‘O’ ( $303^{\circ}\text{C}$ ) corresponds to fixed composition of 2.6% Ag & 97.4% of Pb. This composition is eutectic (lowest melting mixture).

## Curve BO ( Freezing point curve of Pb)

It represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it.

Point ‘B’ is the melting point of pure Pb ( $327^{\circ}\text{C}$ ).

Along BO, the melting point of Pb gradually falls on addition of Ag, till the lowest point ‘O’ is reached where the solution gets saturated with respect to Ag & the melting point of Pb does not fall further.

On cooling the solution, the whole mass having eutectic composition crystallizes out.

$$F = C - P + 1 = 2 - 2 + 1 = 1 \text{ (Univariant)}$$

## Point ‘O’ (Eutectic Point)

The two curves AO & BO meet at O, where three phases (solid Ag, solid Pb & their solution (liquid Ag+Pb)) co-exist. According to condense /reduced phase rule,

$$F = C - P + 1$$

$$= 2 - 3 + 1$$

= 0 ( system is non-variant)

The point ‘o’ represents a fixed composition(Ag=2.6%, Pb=97.4%) & temperature  $303^{\circ}\text{C}$ .

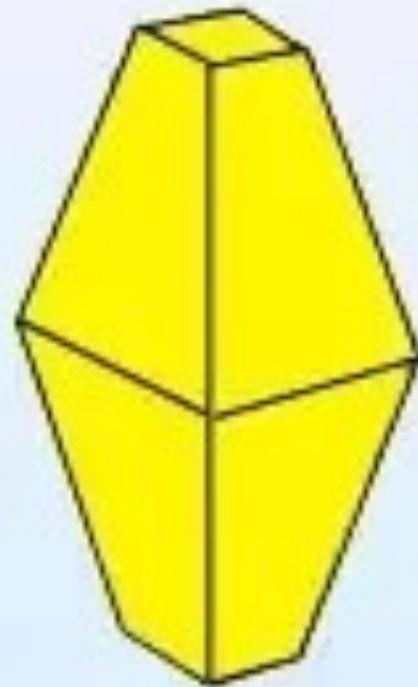
# Applications of phase rule

- 1) It provides convenient basis for classification of equilibrium states of systems with the help of phases, components & degree of freedom.
- 2) It applies to macroscopic system & hence information about molecular structure is not essential.
- 3) Phase rule does not consider the nature or the amount of substances present in the system.
- 4) It helps in predicting the behaviour of a system under different conditions of governing variables.

# Limitations of phase rule

- 1) Phase rule can be applied only for systems in equilibrium. It is not of much help for the system which attains equilibrium slowly.
- 2) All the phases of the system must be present under the same conditions of temp, pressure & gravitational force.
- 3) It considers only the number of phases & not their quantities.
- 4) It applies only to a single equilibrium state & does not indicate the other possible equilibria in the system

## allotrops of sulfur (S<sub>8</sub>)



Above 96<sup>0</sup>C  
↔  
Above 96<sup>0</sup>C



Rhombic

Monoclinic

.....

Q. What is triple point? Explain the triple point with reference to water system.

Ans. Refer Section 4.3 (C).

. How many degrees of freedom are present in the following systems?

- (i) A gas in equilibrium with its solution in a liquid.
  - (ii) A solution of a solid in a liquid in equilibrium with solvent vapour.
  - (iii) Two partially miscible liquids in the absence of vapour.
  - (iv)  $I_2(s) \rightleftharpoons I_2(g)$
  - (v)  $NH_3(g)$ .
- (i) 2, (ii) 2, (iii) 2, (iv) 1, (v) 2.

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Ans. Refer Section 4.3.

December 2011

1. Explain the application of phase rule to one component system.

Ans. Refer Section 4.3.

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June 2012

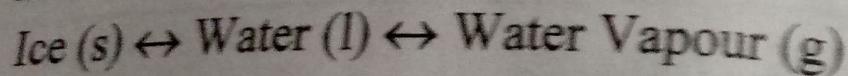
1. Explain application of Gibbs Phase Rule to one component system-water system.

Ans. Refer Section 4.3.

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2. Using phase rule, find the number of degrees of freedom in the following systems at equilibrium.

(i) In the water system when



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(ii) A gaseous mixture of Nitrogen and Hydrogen.

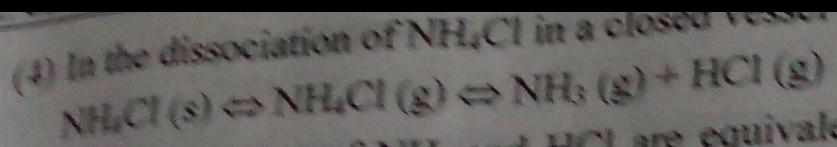
Ans. (i) 0, (ii) 3.

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December 2012

1. State limitations of phase rule.

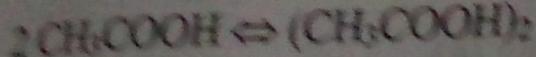
Ans. Refer Section 4.6



The proportions of  $\text{NH}_3$  and  $\text{HCl}$  are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of  $\text{NH}_4\text{Cl}$  alone. Hence, the number of component is one. However, if  $\text{NH}_3$  or  $\text{HCl}$  is in excess, the system becomes a two component system.

- (5) The acetic acid system is a one component system because the composition of each phase can be expressed in terms of each phase of  $\text{CH}_3\text{COOH}$ , although it exists in the form of double molecules entirely in the solid state, to a great extent in the liquid state and only to a smaller extent in the vapour state.

There may be equilibrium such as:



in the solid and liquid phases due to association, but the only independent species in all the three phases is  $\text{CH}_3\text{COOH}$ .

- (6) In the equilibrium,



The minimum components required to express the composition of each phase is three. So it is three component system.

- (7) A salt solution is a two component system.

- (5) A solution of a substance in a solvent consists of one phase.  
For example: glucose solution in water.
- (6) A system containing  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{CO}_2$  has three phases – two solid phases and one gaseous phase.  
 $\text{CaCO}_3 \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$
- (7) A homogeneous solid solution of salt constitutes a single phase.  
For example: Mohr's salt  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$  solution constitutes a single phase although it consists of  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ .
- (8) Each solid makes up a separate phase except in the case of a solid solution. For example, many forms of sulphur can exist together and all are separate phases.

## 4.2.2 Component

The components of the system do not represent the number of the constituent chemical individuals present in the system. As given in the following table:

May 2015

1. Define Phase, Component and Degree of freedom.  
Ans. Refer Section 4.2.1, 4.2.2 and 4.2.3.
2. State Gibbs phase rule. Give its applications to one component system.  
Ans. Refer Section 4.2 and 4.3.
3. What is a condensed phase system? Draw the phase diagram of liquid water with proper labeling.  
Ans. Refer Section 4.4.1 and 4.4.4.

December 2015

1. What is Triple point? Explain it with reference to water system.  
Ans. Refer Section 4.3.
2. What is the phase rule? Draw a neat labeled diagram for water system. Using phase rule find the number of degrees of freedom for the following:
  - (a) Ice(s)  $\leftrightarrow$  Water (l)  $\leftrightarrow$  Water Vapour (g).
  - (b) Water(l)  $\leftrightarrow$  Water Vapour (g).  
Ans. Refer Section 4.2 and 4.3.
3. Discuss the limitations of phase rule.  
Ans. Refer Section 4.6.

May 2016

1. Give the number of phases in the following systems.
  - (a) Saturated solution of NaCl
  - (b) Mixture of rhombic and mono-clinic sulphur
  - (c) Mixture Oxygen and Nitrogen
  - (d) Ice  $\leftrightarrow$  Water