

## MODULE 4. PHASE RULE

### INTRODUCTION

Phase Rule was deduced on the basis of “Thermodynamic principles” by Willard Gibbs (1876) and was later developed by Ostwald, Van't Hoff, H.W.B. Roozeboom and many more. Phase rule is an important tool in the study of *heterogeneous equilibrium*. It relates the conditions which must be specified to describe the state of a system at equilibrium. The plot indicating the relationships between various phases under different temperature, pressure and concentration is known as **phase diagram**. **Phase rule**, with the help of a **phase diagram**, is useful in predicting the effects of temperature, pressure and concentration on the equilibrium of *heterogeneous systems*.

A substance can exist in various states depending on the external conditions. For example, water can exist in the form of solid, liquid and vapour. A change in the state of a substance is called **phase transition**. Equilibrium in a system in which phase transitions occur in addition to a chemical process is called phase equilibrium.

**GIBB'S PHASE RULE** states that in every heterogeneous system at equilibrium, the sum of the number of phases and degree of freedom is greater than the number of components by 2, provided the equilibrium between any number of phases is not influenced by gravity, electrical or magnetic forces or by surface action, and is only influenced by temperature, pressure and concentration. It can also be expressed as:

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

Where, P = number of phases, C = number of components, and F = degrees of freedom.

**Phase:** is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other parts of the system by definite bounding surfaces. **Examples:**

- (i) In a freezing water system, ice, water and water vapour are the three phases which are physically distinct and homogeneous  $\text{Ice(s)} \leftrightarrow \text{Water (l)} \leftrightarrow \text{Water vapour (g)}$
- (ii) A gaseous mixture, which is thoroughly miscible in all proportion, consists of a single phase.
- (iii) If two liquids are miscible, they will form one liquid phase only.
- (iv) Thermal decomposition of  $\text{CaCO}_3$  (chalk) consists of three phases namely, two solids and one gaseous.  $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$ .
- (v) A mixture of CaO and  $\text{CaCO}_3$  consists of two phases.
- (vi) Two immiscible liquids like water and oil will form two separate phases.

**Component:** is the smallest number of independent variable constituents taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation. The components do not represent the number of constituents or chemical individual present in the system.

**Examples:**

- (i) In water system, the phases present are three viz., ice, water and water vapour. The composition of each phase can be expressed by a single component,  $\text{H}_2\text{O}$ . Hence it is a one component system.
- (ii) In sulphur system there are four phases eg. Rhombic, monoclinic, liquid and sulphur vapours are present. Each phase can be regarded as being made of sulphur. Hence it is a one component system.
- (iii) A system of saturated solution of NaCl consists of solid salt and salt solution. The chemical composition of all the two phases can be expressed in terms of NaCl and  $\text{H}_2\text{O}$ . Hence it is a two component system.
- (iv) In the thermal decomposition of  $\text{CaCO}_3$ , the following equilibrium exists.  $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$

The system consists of three phases namely solid  $\text{CaCO}_3$ , solid CaO and gaseous  $\text{CO}_2$ . The system has three constituents, but is considered as a two component system because the composition of each phase can be expressed in terms of any two of the constituents.



(v) In the dissociation of  $\text{NH}_4\text{Cl}$  in a closed vessel,  $\text{NH}_4\text{Cl}(\text{s}) \leftrightarrow \text{NH}_4\text{Cl}(\text{g}) \leftrightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ , 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.

(vi) 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:  $2 \text{CH}_3\text{COOH} \leftrightarrow (\text{CH}_3\text{COOH})_2$  in the solid and liquid phases due to association, but the only independent species in all the three phases is  $\text{CH}_3\text{COOH}$ .

(vii) In the equilibrium,  $\text{Fe}(\text{s}) + \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{FeO}(\text{s}) + \text{H}_2(\text{g})$ , the minimum components requires to express the composition of each phase is three. So it is three component systems.

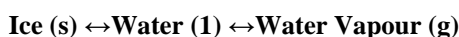
(viii) A salt solution is a two component system.

**Degree of Freedom or, Variance:** means the minimum number of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to describe completely the state of the system. A system having **one, two, three or zero** degrees of freedom are usually called **univariant, bivariant, trivariant and invariant or non-variant** respectively. Common examples include:

- (1) In case of water system, **Ice (s)  $\leftrightarrow$  Water (l)  $\leftrightarrow$  Water Vapour (g)**, no specification of conditions is necessary because the three phases can occur in equilibrium only at a particular temperature and pressure. This situation exists only at triple point; hence this system does not have any degree of freedom (invariant). If condition (e.g. pressure or temperature) is altered, three phases will not remain in equilibrium and one of the phases will disappear.
- (2) Consider a system containing water in contact with its vapour. **Water (l)  $\leftrightarrow$  Water Vapour (g)**  
The vapour will exert a certain pressure at a particular temperature. Hence, it is enough if we fix the temperature of the system. Then, the pressure that would be exerted by the vapour is automatically fixed. Hence of the two variable factors of temperature and pressure, it is enough if we fix one. Therefore this system has only one degree of freedom or it is univariant.
- (3) A system of a pure gas should satisfy the gas equation  $PV = RT$ . If we assign values arbitrarily for any two of the three variables, the value of the third gets automatically fixed and the system is completely defined. This system has two degrees of freedom or it is bivariant.
- (4) For a system consisting of  **$\text{NaCl}(\text{s}) \leftrightarrow \text{NaCl Water}(\text{aq})$**  is completely defined if the temperature or pressure is specified. The saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

#### APPLICATION OF PHASE RULE TO ONE COMPONENT SYSTEM

**The Water System:** Water is the most common example of one component system. The water system consists of three phases, namely, ice, water and water vapour.



The three phases may occur in four possible combinations in equilibrium as follows:

- (i) Liquid  $\leftrightarrow$  Vapour

(ii) Liquid ↔ Solid

(iii) Solid ↔ Vapour

(iv) Solid ↔ Liquid ↔ Gas

As water (H<sub>2</sub>O) is the only compound involved in the system, therefore, it is single or one component system. From the phase rule, when  $C = 1$ ,

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

The degree of freedom depends on the number of phases present at equilibrium. Three different cases are possible.

- (i)  $P = 1$ ;  $F = 2$  (bivariant system)
- (ii)  $P = 2$ ;  $F = 1$  (univariant system)
- (iii)  $P = 3$ ;  $F = 0$  (invariant system)

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) is drawn and resulting phase diagram is shown in Fig:

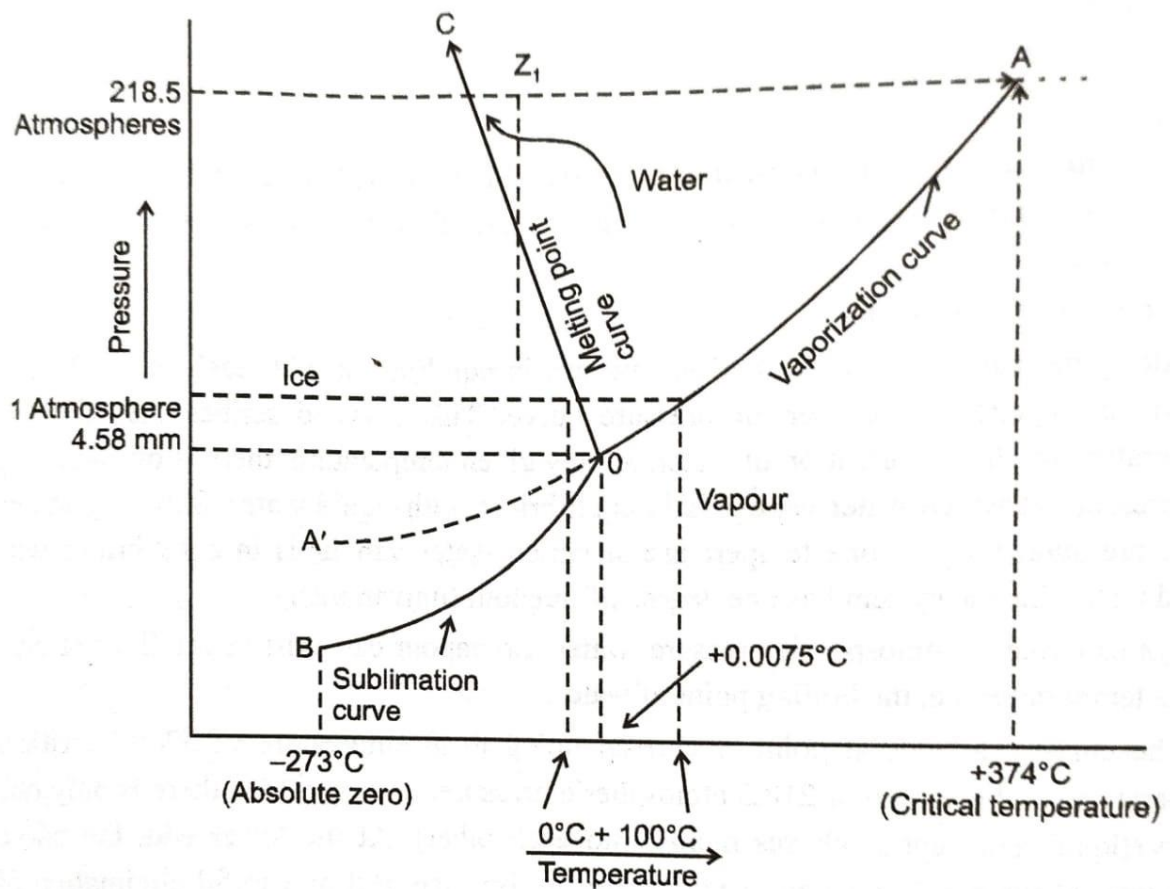


FIG: Phase Diagram of Water System

**(A)Areas:** As can be seen from the diagram, there are three areas namely **BOC (ice), COA (water) and 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 and pressure should be fixed. So the system in an area has two degrees of freedom (bivariant). The same conclusion is drawn by substituting the values of **C = 1 and P = 1** in the phase rule equation:

$$F = C - P + 2, \text{ i.e } F = 1 - 1 + 2, F = 2$$

Similarly, all the areas are bivariant in nature

#### **(B) Boundary Lines or Curves:**

These areas are separated by lines OA, OB, OC and OA' which connect the point at which two phases can co-exist in equilibrium. In order to locate any point on particular line, either temperature or pressure co-ordinate should be known. In other words, if the value of either the temperature or the pressure is fixed, the value of the other is automatically fixed and the system is completely defined. Any point on the boundary lines has one degree of freedom or is univariant.

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

- (1) **Curve OA (Vaporization Curve)** : Separates the liquid region from vapour region and is known Vaporization curve of water. At any given temperature, there is only one value of pressure at which water vapour is in equilibrium with liquid water and vice versa. Just above the curve the liquid is the stable phase, while below this vapour is the stable phase. The curve OA has an upper limit at 374° C and 218 atm. which is the critical point beyond which the liquid phase merges in to vapour phase and are no longer distinguishable.
- (2) **Curve OB (Sublimation Curve)**: represents the variation of vapour pressure of solid with temperature. This is the sublimation curve where, solid and vapour are in equilibrium. The curve terminates at B, at – 273° C temperature (absolute zero), beyond which the two phases merge into each other.
- (3) **Curve OC (Melting or Fusion Curve)**: the melting (fusion) curve which divides the solid from liquid region. The curve indicates the influence of pressure on the melting point of ice. The curve starts from O and extend to very high values of pressure. The slope of the curve is negative implying that the melting point is lowered by the increase of pressure or ice melts with a decrease in volume.

**(C) Metastable Curve (OA'):** This is called as the super cooling curve. It is an extension of the vapour pressure curve OA. This shows that, it is possible to super cool water several degrees below its freezing point if the system is perfectly clean. The super cooled system is unstable, that is metastable. On a slight disturbance the super cooled water at once changes to ice or vapour.

**(D) Triple Point:** It has been found experimentally that the **curves OA, OB and OC meet in a point 'O'**. This is called the 'triple point where all the three phases' i.e, ice, water and vapour coexist. Only at a particular value of temperature and pressure represented by the triple point, all the **three phases can co-exist**. So, the system has **no degrees of freedom** (invariant) at this point. The triple point corresponds to a temperature **of 0.0075°C and a pressure of 4.58 mm**. At this point, if we change either temperature or pressure, one of the phases will disappear. **F = 3 - 3 = 0**. This means the degree of freedom is zero, i.e; neither pressure nor temperature can be changed without causing the disappearance of one of the phases. If either temperature or pressure is changed even slightly, one of the three phases disappears and the system changes from non-variant to univariant.

The salient features of the phase diagram of the water system are summarized in Table (Number of component= 1)

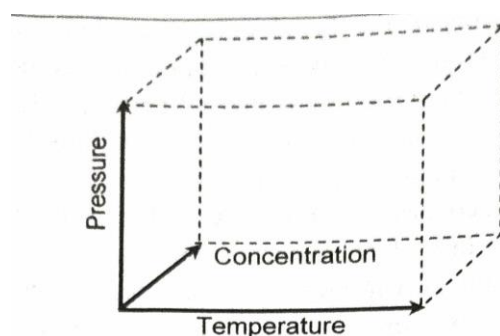
| Name of the system as represented in the phase diagram                                    | Phase in equilibrium                                | Degree of freedom or variance (F=C-P + 2)  |
|---|---|--|
| <b>Areas</b>  |   |  |
| (1) BOC (ice)<br>(2) COA (water)<br>(3) AOB (vapour)                                      | Ice<br>Water<br>Vapours                             | Two<br>(Bi-variant)<br>$F = 1 - 1 + 2 = 2$ |
| <b>Curve</b>  |   |  |
| (1) OC (Melting point curve)<br>(2) OA Vaporization curve)<br>(3) OB ( Sublimation curve) | Ice and water<br>Water and Vapour<br>Ice and Vapour | One<br>(univariant)<br>$F = 1 - 1 + 2 = 1$ |

|                               |                     |                                      |
|-------------------------------|---------------------|--------------------------------------|
| <b>Point</b> O (Triple Point) | Ice, Water, Vapours | Zero (Invariant) $F = 1 - 3 + 2 = 0$ |
|-------------------------------|---------------------|--------------------------------------|

## APPLICATION OF THE PHASE RULE TO TWO COMPONENT SYSTEMS

### General Characteristics of Two Component Systems:

- (1) The two component systems have three variables namely pressure, temperature and concentration.
- (2) The composition of all the individual phases of the system can be expressed by means of not less than two components.
- (3) The maximum number of phases in a two-component system will be four,  $P = C - F + 2$ ,  $P = 2 - 0 + 2$ ,  $P = 4$  (Maximum number of phases exist when degrees of freedom = 0. Negative degree of freedom cannot exist).
- (4) The maximum number of degrees of freedom in a two component system will be three.  $F = C - P + 2$ ,  $F = 2 - 1 + 2$ ,  $F = 3$  (I.e. when the system exists as a single phase).
- (5) For constructing a phase diagram of a two component system, a three dimensional space model is required using the three variables (viz, temperature, pressure and concentration) as its co-ordinates.



**Fig: Three dimensional space model of a two component system**

To simplify the diagram, one of the variables is kept constant. If the pressure is kept constant, the diagram is called isobaric; if temperature is kept constant it is called isothermal and if composition is kept constant, the diagram is called isoplethal.

**Phase rule for two component system:** In a two-component system, when  $P = 2$ , degree of freedom ( $F$ ) has the highest value i.e. 3. Three variables temperature, pressure and concentration of one of the two components must be specified in order to describe the system completely. Since the maximum number of degrees of freedom in a two component system is 3, the phase behaviour of a binary system may be represented by a three dimensional diagram of pressure, temperature and composition. Solid-liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is small on this type of equilibrium. Usually the experiments are conducted under atmospheric pressure. Thus keeping the **pressure constant** of a system, in which **vapour phase is not considered**, is known as **condensed system**. It will reduce the degrees of freedom of the system by one. For such a system the phase rule becomes  $F = C - P + 1$ . This is known as the **reduced or condensed phase rule**, having only two variables, temperature and concentration (composition) of the constituents.

**Phase Rule to Two Component System: (Pb-Ag System):** It is a two-component system with four possible phases- solid Ag, solid Pb, solution of Ag + Pb and vapour. Since the boiling points of Pb and Ag being considerably high, the vapour phases is practically absent so the pressure has nearly no effect on equilibrium, so the system can be conveniently represented by a temperature- concentration diagram at constant atmospheric pressure. As the gaseous phase is practically absent and one variable pressure is neglected, the condensed phase rule:  $F = C - P + 1$  will be applicable.

**The diagram consists of:**

(1) **Curve AO (Freezing curve of Ag):** It shows the effect on freezing point of Ag on addition of Pb in small quantities. It starts from A (961°C), the melting point of Ag where pure Ag coexists as solid and liquid. The curve indicates that the melting point of Ag falls gradually on adding Pb, along AO till the lowest point O (303°C) is reached, where the solution gets saturated with Pb. Along this curve solid Ag and solution coexists and hence according to condensed phase rule,  $F = 3 - P = 3 - 2 = 1$ , i.e., the system is univariant. The point O corresponds to a fixed composition of 2.6 % Ag and 97.4 % Pb is known as **eutectic composition**

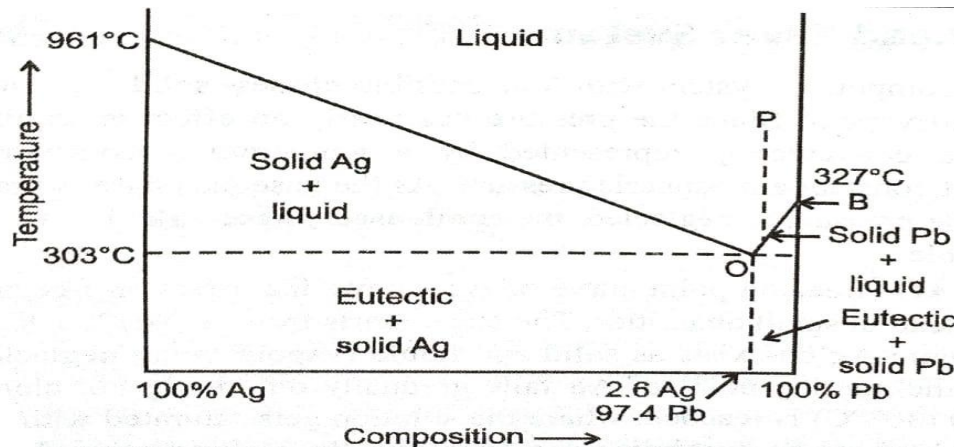


Fig. 4.4 : T – C diagram of Pb-Ag system

(2) **Curve BO (Freezing point curve of Pb):** It represents the effect on freezing point of Pb on gradual addition of small quantities of Ag to it. Point B is the melting point of pure Pb (327°C). Along BO melting point gradually falls on adding Ag till the lowest point O is reached, where the solution gets saturated with respect to Ag. On cooling the whole mass crystallises out. The system is univariant.

(3) **Point O (Eutectic point):** The two curves AO and BO meet at O, where three phases (solid Ag, solid Pb and their solution) co-exists and according to reduced phase rule the system will be invariant; The point O represents a fixed composition and is called **eutectic composition**. No mixture of Pb and Ag has a melting point lower than the eutectic temperature. Further cooling results in the simultaneous crystallization of mixture of Ag and Pb.

**Eutectic System:** A binary system consisting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically, is known as the "eutectic system", for example, a mixture of lead and silver comprises of such a system. **Eutectic mixture** is a 'solid solution of two or more substances having the lowest freezing point of all the possible mixture of the components. It is utilised in "alloying of low melting point", which are generally eutectic mixtures.

**Eutectic point:** Two or more solid substances capable of forming solid solutions with each other have the property of lowering each other's freezing point; and the minimum freezing point attainable corresponding to the eutectic mixture, is termed as the eutectic point (means lowest melting point).

**Application of eutectics:** Low melting alloy are used in safety devices (for example, as plugs in automobiles), fire-sprinklers and as 'fail safe' device in boilers). By suitable choice of metals, very low melting alloys can be obtained, for example, Wood's metal alloy containing 50% Bi, 25% Cd and 12.5% Sn melts at 65°C only.

(4) **Area ACB:** It represents the solution of Pb-Ag. If a sample of Pb containing less than 2.6 % Ag is taken, say x. On allowing it to cool, the temperature gradually falls without any change in composition, till y is reached on the curve BC. On lowering the temperature Pb begins to separate out and the composition varies along yO, till point O is reached. On further cooling, the whole mass solidifies.

**Applications of Phase Rule:** are as follows:

- (1) It applies to physical as well as chemical phase reactions.
- (2) It provides a convenient basis for classification of equilibrium states of systems with the help of phases, components and degree of freedom.
- (3) It applies to macroscopic systems and hence information about molecular structures is not essential.

- (4) Phase rule does not take any cognizance of the nature or the amounts of substances present in the system.
- (5) It indicates that different systems having the same degree of freedom behave in a similar fashion. Further, it helps in predicting the behaviour of a system under different conditions of the governing variables.
- (6) It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter-converted or eliminated.

**Limitations of the Phase Rule are as follows:**

- 1. Phase rule can be applied only for systems in equilibrium. It is not of much help in case of systems which attain the equilibrium state very slowly.
- 2. All the phases of the system must be present under the same conditions of temperature, pressure and gravitational force.
- 3. It applies only to a single equilibrium state. It does not indicate the other possible equilibrium in the system.
- 4. Phase rule considers only the number of phases but not their quantities. Even a minute quantity of the phase, when present, accounts towards the number of phases. Hence much care has to be taken in deciding the number of phases existing in the equilibrium state.
- 5. The solid and liquid phases should not be so finely subdivided as to bring about deviation from their normal values of vapour pressure.