

Phase diagrams are of considerable significance both industrially and commercially, particularly for steels, ceramics, semiconductors. They are basis of separation procedures in petroleum industry, food formulations and in the preparation of cosmetics.

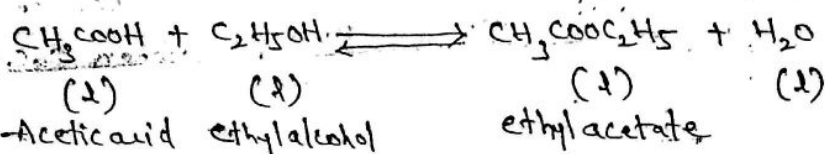
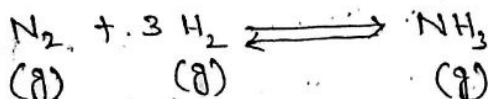
Phase rule predicts quantitatively the equilibrium existing between different phases of a heterogeneous systems.

System:- A system refers to a part of space filled with a substance or mixture of substances and isolated from the surrounding medium. It may include only one phase or more than one phases.

System is divided into 2 types depending upon the chemical reaction.

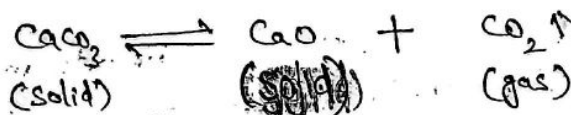
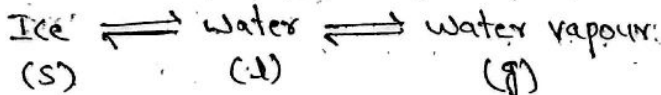
(a) Homogeneous system:- A system consisting of only one phase at equilibrium, it is called homogeneous system.

Ex:-



(b) Heterogeneous system:- A system consisting of 2 or more phases at equilibrium, it is called heterogeneous system.

Ex:-



The phase rule requires a careful use of terms. It contains mainly the 3 important terms namely phase, component and Degree of freedom or degree of variance.

(A) Phase (P):- A phase is defined as "a homogeneous, physically distinct and mechanically separable portion of system, which is separated from other homogeneous parts of the system by definite boundary surface".

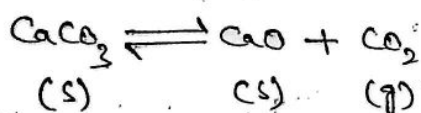
Ex: In a beaker, the freezing water system contains 3 phases, viz Ice (solid), water (liquid), and water vapour (gas) in equilibrium.

(2) Air is the most common example of one phase system (air which is a mixture of  $N_2$ ,  $O_2$ ,  $CO$ , water vapour, noble gases).

(3) Mixture of 2 or more gases and a mixture of 2 or more miscible liquids are homogeneous. So in such systems, phase is one, i.e.,  $P=1$ . A system consisting of only one phase is said to be homogeneous. Glucose in water,  $NaCl$  in water, and ethanol in water possess one phase.

(4) Two immiscible liquids, two solids, solid + gas, solid + liquid and liquid + gas constitute 2 different phases. For example when  $C_6H_6$  and water are mixed, they form 2 distinct layers, which are physically distinct and mechanically separable, so in such systems, phases are 2; i.e.,  $P=2$ .

(5) In case of solids each solid constitutes one phase. For a mixture of solids, there will be as many phases as the number of solids present in a system at equilibrium. For example, when  $CaCO_3$  is heated it decomposes giving  $CaO$  and  $CO_2$ .



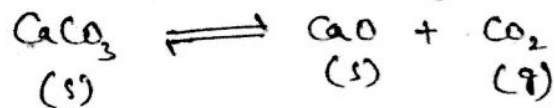
At the equilibrium, we have 2 solid phases and one gaseous phase. So, in such system phase is 3; i.e.,  $P=3$ .

B) Components (C): It is defined as "Number of components in a system is the smallest number of independently variable constituents by means of which the composition of every possible phase in the system can be expressed with a chemical formula". It is denoted by 'C'.

To express the composition of the phases, coefficients like '+', '-' or 'zero' can be used before the components.

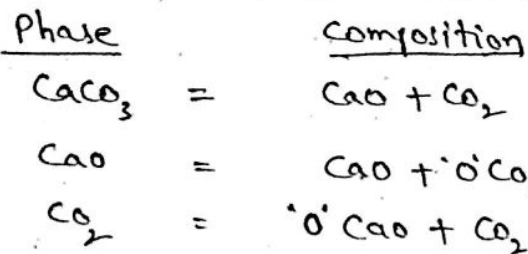
Q-1) In water system, the composition of each phase namely ice, water or water vapour is given by a single formula  $H_2O$ . So the number of components of water system is 'one' i.e.,  $C=1$  and it belongs to single or one component system.

Ex: (ii) Consider another heterogeneous equilibrium.

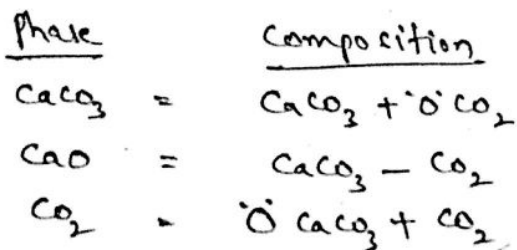


In the above chemical equilibrium, there are 3 phases, i.e., 2 solid phases and one gaseous phase. The number of independently variable constituents are '3'. But the composition of each phase can be expressed in terms of any two of the constituents making the quantity of one of the 3 either 'zero' (or) '+' (or) '-' according to need. Hence it is a 'two' component system, i.e.,  $C = 2$ .

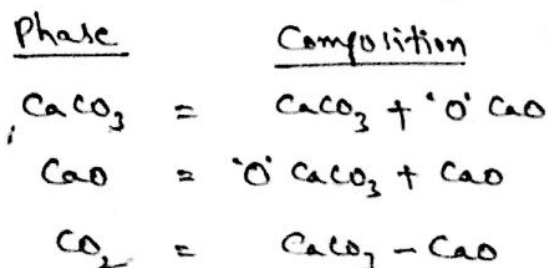
(a) If the constituents chosen are CaO and  $\text{CO}_2$ .



(b) If the constituents chosen are  $\text{CaCO}_3$  and  $\text{CO}_2$



(c) If the constituents chosen are  $\text{CaCO}_3$  and CaO



Since at least 2 out of 3 constituents are required to represent the composition of all the phases, the system is a 'two component system', i.e.,  $C = 2$ .

(C) Degree of freedom (or) Degree of variance:- (F)

Pressure, Temperature and Concentration (composition) of the phase are the factors which can affect the equilibrium of a system.

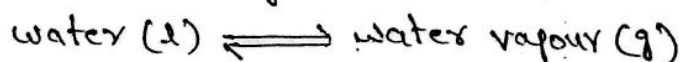
⤵ The minimum no. of the variable factors, such as T, P and Composition of the phases, which must be arbitrarily fixed in order to define condition of the system completely is termed as Degree of freedom (or) variance.

The degrees of freedom of a system may be one, two, three (or) zero are known as uni variant (mono variant), bi variant, tri variant & non variant systems respectively.

Ex (i) In case of water system,  $\text{Ice (s)} \rightleftharpoons \text{water (l)} \rightleftharpoons \text{water vapour (g)}$

If all the 3 phases are present in equilibrium, then no condition need to be specified, as the 3 phases can be in equilibrium only at particular temperature ( $0.0098^\circ\text{C}$ ) and pressure ( $4.58 \text{ mm}$ ). The system is therefore, zero variant (or) non-variant (or) invariant (or) has no degree of freedom, i.e.,  $F=0$ . If condition (ext temp, pressure) is altered, three phases will not remain in equilibrium and one of the phases disappears.

(ii) For a system consisting of water in contact with its vapour,



we must state either the temperature (or) pressure to define it completely. Hence, degree of freedom is one (or) system is univariant i.e.,  $F=1$ .

(iii) For a gaseous mixture of  $\text{N}_2$  and  $\text{H}_2$ , we must state both the pressure and temperature, because if P & T are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has 2 degrees of freedom (or) system is bivariant i.e.,  $F=2$ .

## Phase Rule:-

For the study of the behaviour of the heterogeneous system an important generalisation was put forward by willard Gibbs (American physicist) known as "phase rule" is applicable to all heterogeneous systems in equilibrium without any exception.

It states that "when the heterogeneous equilibrium between different phases is not influenced by gravitational forces, electrical forces or by magnetic forces, but only by temperature, pressure and composition, the sum of the number of phases ( $P$ ) and the number of degrees of freedom ( $F$ ) always exceeds the number of components ( $C$ ) by 2". The relation is as follows.

$$F + P = C + 2$$

(or)

$$F = C - P + 2$$

## Uses of Phase rule:-

1. Phase rule provides a convenient basis for classification of system with the help of phases, components, degrees of freedom.
2. The phase rule indicates that different systems having same degrees of freedom behave in a similar fashion.
3. It is applied to macroscopic systems, hence information about molecular structures is not required.

## Limitations:-

1. The phase rule can be applied only for systems in equilibrium. It is not applicable to systems which attain equilibrium at a later stage.
2. All the phases must be present under same conditions of temperature and pressure.
3. Only three degrees of freedom are allowed to influence the equilibrium system.

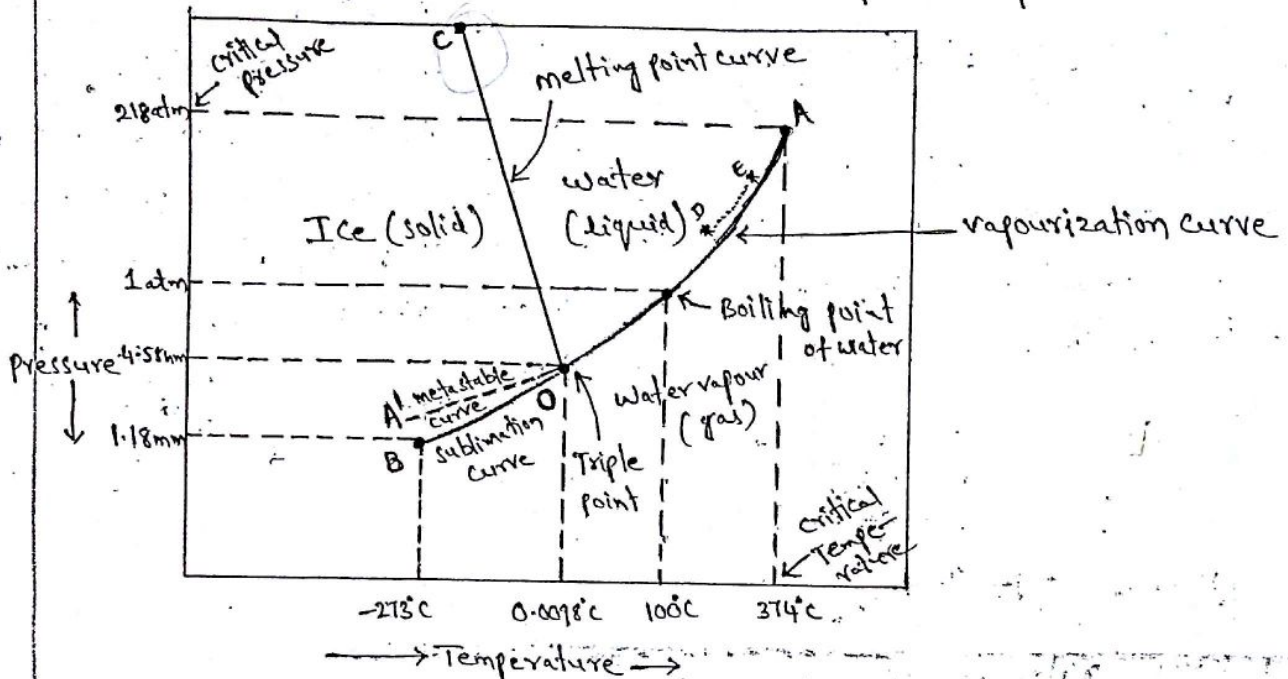
## Phase Diagram:- (Equilibrium Diagram)

It may be defined as a plot showing the conditions of pressure and temperature (or temperature and composition) under which 2 or more physical states of a system can exist together in a state of dynamic equilibrium.



## One Component system:- (Water system)

Under normal conditions the system 'water' is a three-phase, one component system. In this system  $\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour}$  exists in equilibrium. All the 3 phases can be represented by one chemical formula ' $\text{H}_2\text{O}$ '; hence it is a one component system.



### \* Phase diagram for water system \*

The phase diagram of water system consists of three important features, namely lines (or) curves, Regions (or) areas and Triple point.

(1) Lines (or) curves:- The phase diagram of water system consists of 4 curves OA, OB, OC and OAB.

(a) OA curve:- This is the vapour pressure curve of water. It represents the equilibrium between liquid water and water vapour at different temperatures. The starting point of the curve is 'O' and ends at 'A'. To analyse the curve, consider any point on the curve. For a fixed value of pressure, temperature has also a fixed value. So, to define the system, completely at any time, it is necessary to mention either pressure (or) temperature. Thus water vapour system is univariant (or) has one degree of freedom. It may also be shown by phase rule equation.

$$P = 2 \text{ (water, vapour)} ; C = 1$$

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

$$F = 1.$$

$$C = C - P + 2$$

[B4]

(b) OB curve:- This is the sublimation curve of Ice. It represents the equilibrium between ice and vapour at different temperature. The starting point of the curve is 'O' and ends at 'B'. From the diagram it is obvious that for a particular temperature there can be only one pressure. Similarly, for each pressure, there is only one temperature at which both the phases co-exist. Thus, ice, vapour system is univariant or has one degree of freedom. It may also be shown by the phase rule equation.

$$P=2; C=1$$

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

$$F = 1.$$

(c) OC curve:- This is the melting point curve of Ice. It represents the equilibrium between ice and water. The starting point of the curve is 'O' and ends at 'C'. It is to be noted that the line 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. At any point of the curve two phases are in equilibrium. This system is univariant system or has one degree of freedom. It may also be shown by phase rule equation.

$$P=2; C=1$$

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

$$F = 1.$$

(d) OA' curve:- The dotted curve OA' is a continuation of the OA curve and represents the vapour pressure (vapourization) curve of supercooled water. This curve is known as metastable curve. When slight disturbance is there, the supercooled phase at once changes to solid, ice and the curve merges into OB.

(2) Areas (or) Regions:- The phase diagram of water system has 3 regions namely AOB, AOC and BOC.

(a) AOB curve:- represents water vapour phase only.

(b) AOC curve:- represents liquid water phase only.

(c) BOC curve:- represents ice phase only.

Consider a point 'D' in the area AOC. By increasing both 'T' and 'P' simultaneously it moves to another point 'E' in the same area (AOC). There is no change in the number of phases even though two variables are changed simultaneously. Thus 'P' and 'T' are the 2 quantities to define the system completely at any point in area. So the system represented by area has two degree of freedom or bivariant. According phase rule,

$$C = 1 \quad P = 1$$

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

$$F = 2$$

3) Triple point:- (O).

In water system, it is the point where the 3 curves OA, OB and OC meet together. At this point, all the 3 phases are in equilibrium. At point 'O' temperature and pressure are fixed at  $0.0098^\circ\text{C}$  and  $4.58 \text{ mm}$  respectively. Since on changing either, temperature or pressure, one of the phase disappears. So the system has zero degree of freedom, or invariant at the point 'O'. This can be shown by phase rule equation also,

$$C = 1 \quad P = 3$$

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

$$F = 0$$



## Two - Component system:-

In a two component system the composition of all the individual phases available in various phase equilibria are expressed with the help of 2 components.

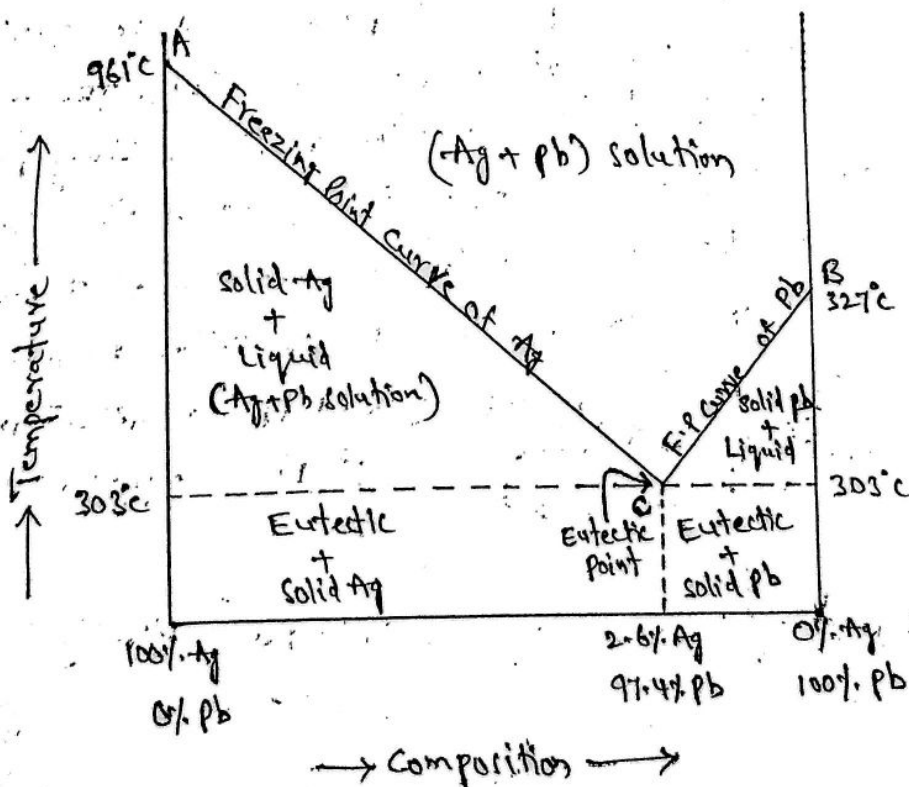
Ex:- (Ag-Pb) system, (NaCl-H<sub>2</sub>O) system, (Mg-Zn) system

In a solid-liquid equilibrium, the gas phase is usually absent and the effect of pressure on the equilibrium is negligible such a system when the pressure variable is kept constant is called Condensed system. Since the degree of freedom for a Condensed system is reduced by one, it is known as 'reduced phase equation' and can be written as,

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

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

## Silver - Lead system:- (Ag + Pb) System



The phase diagram of this (Ag-Pb) system consists of 2 curves AC and BC intersecting at the point 'c' (eutectic point) and ACB region or area.

- a) Curve AC:- The melting point of silver is  $961^{\circ}\text{C}$ . The continuous addition of Pb in it, lowers the melting point along AC. The point 'A' is the melting point of pure silver. The melting point of silver falls gradually with the addition of lead along AC. The lowest point is attained at 'c'. At point 'c', the solution becomes saturated with respect to lead and if any more lead is added, it separates out as a solid. AC curve is called the Freezing point curve of silver. Two phases co-exist (solid Ag + solution) in equilibrium along AC. Thus according to reduced phase eqn the system along the AC curve is "univariant".

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

$$F' = 2 - 2 + 1 \quad [\because C=2; P=2 \text{ (solid Ag, solution)}]$$

$$F' = 1$$

- b) BC curve:- The melting point of pure lead is  $327^{\circ}\text{C}$ . The point B represents the melting point of pure lead (Pb). The melting point of Pb falls gradually with the addition of silver along BC. The lowest point is attained at 'c'. At the point 'c', the solution becomes saturated with respect to Ag, and further addition of silver results in its separation as a solid. Curve BC is called Freezing point curve of lead. Two phases co-exist (solid Pb + solution) in equilibrium along BC. Thus according to reduced phase equation the system along the BC curve is univariant.

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

$$F' = 2 - 2 + 1 \quad [\because C=2, P=2 \text{ (solid Pb, solution)}]$$

$$F' = 1$$

[6]

(c) ACB region:- In this region, only the (Ag+Pb) solution exists i.e., there is only one phase and hence it has 2 degree of freedom viz, temperature and composition. For any composition and temp. in this region, the melt (solution) of Ag and Pb is stable

$$C=2, P=1$$

$$F' = C - P + 1 = 2 - 1 + 1 = \underline{2}$$

(d) Point 'c':- [Eutectic point]

It is the point at which the curves AC and BC meet together. At this point, 3 phases (solid Ag, solid Pb and their solution) co-exist. Therefore, point 'c' has no degree of freedom, i.e., it is invariant. This is also in accordance with the reduced phase equation

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

$$F' = 2 - 3 + 1 \quad (\because C=2; P=3)$$

$$F' = \underline{0}$$

In (Ag-Pb) system, 'c' point is known as Eutectic point. It is defined as 'the lowest temperature at which the liquid mixture of 2 components can exist and if the liquid is cooled below this temperature, both the components separate simultaneously in the solid form having the same composition as in the solution'.

Eutectic Temperature:- The temperature (305°C) corresponding to Eutectic point is called Eutectic temperature.

Eutectic mixture:- The composition (97.4% Pb and 2.6% Ag) corresponding to Eutectic point is called Eutectic mixture.

Below the temperature line of eutectic temperature, we have



2 regions in the diagram, viz,

- (i) the region marked eutectic + solid Ag, in which crystalline Ag and solid eutectic are stable.
- (ii) the region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

Application of (Ag-Pb) system:- [Pattinson's process of desilverization of

The principle of (Ag+Pb) system is utilized in the pattinson Process of desilverization of lead. If a sample of argentiferrous-lead, containing less than 2.6% Ag, is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver (Pb-Ag) alloy containing Ag greater than 2.6% is allowed to cool, then pure silver separated along the curve AS, till the eutectic composition at 'O' is reached. ✓

Cooling curve of Iron:- (not in syllabus)

Pure iron is ductile and soft. Its melting point is  $1539^{\circ}\text{C}$ . It is an allotropic metal and depending on the temperature it exists in BCC or FCC structures. At room temperature iron is in BCC lattice and at  $910^{\circ}\text{C}$  it changes to FCC and then at  $1400^{\circ}\text{C}$  back to BCC vice-versa. At  $770^{\circ}\text{C}$  called Curie point at which the magnetic properties of iron disappear and iron become non-magnetic until the temperature drops back to curie point then the magnetic properties reappear.

