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# PHASE EQUILIBRIA

## 5.1. INTRODUCTION : DEFINITION OF THE PHASE RULE

A heterogeneous system is defined as a system consisting of a number of phases in equilibrium. The number of phases that can exist together at equilibrium depends upon the conditions of temperature, pressure and concentration of the different phases. As a result of a detailed mathematical and thermodynamic studies of the heterogeneous equilibria, J. Williard Gibbs in 1876 put forward a generalization which is applicable to all systems in equilibrium without any exception. This generalization is known as 'Phase Rule'. It cannot be expressed in words. It is defined by the mathematical equation as under :

"For a heterogeneous system in equilibrium

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

where  $F$  = number of degrees of freedom

$C$  = number of components

and  $P$  = number of phases"

Before we proceed further to take up the studies related to Phase Rule, it is essential to understand the various terms involved. These are discussed in the next section.

## 5.2. EXPLANATION OF THE TERMS INVOLVED

(1) **Phase.** A heterogeneous system consists of various homogeneous parts in contact with each other but with distinct boundaries. The various homogeneous parts, which also have distinct physical and chemical properties and which may, if necessary, be mechanically separated from each other are known as phases.

Hence "a phase may be defined as any part of a system which is (a) homogeneous and separated from other parts of the system by a distinct boundary, (b) physically or chemically different from other parts of the same system, and (c) mechanically separable from other parts of the system"

Examples :

System	Phase
(i) Mixture of gases which do not react.	1 gaseous phase (all gases are completely miscible)
(ii) Ice and water.	2 phases : 1 solid and 1 liquid
(iii) Water and water vapour.	2 phases : 1 liquid and 1 gaseous
(iv) Ice, water and water vapour.	3 phases : 1 solid, 1 liquid and 1 gaseous
(v) Two immiscible liquids, e.g., $\text{CS}_2/\text{H}_2\text{O}$ , $\text{CCl}_4/\text{H}_2\text{O}$ , etc.	2 phases : Both liquid

(vi) Two miscible liquids, e.g., water and alcohol.	1 phase : Only liquid.
(vii) Solid naphthalene and naphthalene vapour.	2 phases : 1 solid and 1 gaseous
(viii) $\text{CaCO}_3$ , $\text{CaO}$ and $\text{CO}_2$ .	3 phases : 2 solids and 1 gaseous
(ix) Monoclinic and rhombic sulphur.	2 phases : Both solids
(x) Saturated solution of common salt containing excess of the salt.	3 phases : Solid salt, solution and water vapour

From the above examples, it is clear that

(i) Miscible gases and miscible liquids constitute a *single phase*.

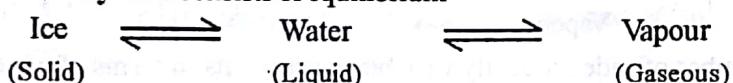
(ii) Solid + liquid, solid + gas, liquid + gas, two solids and two immiscible liquids constitute *two phases*.

(iii) Different solids (except in solutions) are regarded as different phases, howsoever intimately they may be mixed.

**(2) Components.** *The number of components of a system at equilibrium is defined as 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 a chemical equation, negative and zero signs being permitted.*

It is important to note that the components of a system may or may not be the same as the actual substances present in the system i.e., the constituents of the system. Only those constituents of an equilibrium mixture which can undergo *independent variation* are regarded as components. This is explained by the examples given below.

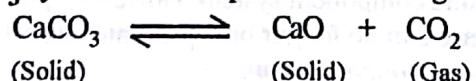
**Examples :** (i) Water system consists of equilibrium



This system consists of one component only i.e., it is a one component system because the composition of each of the three phases present can be directly expressed as  $\text{H}_2\text{O}$ . It may be noted that hydrogen and oxygen are not the components of the system, firstly because in  $\text{H}_2\text{O}$ , hydrogen and oxygen are combined in the fixed ratio (2 : 1), i.e., they are not independently variable and secondly because they are not present as such, in the equilibrium mixture.

(ii) Sulphur system consisting of four phases—Monoclinic(s), Rhombic(s), Liquid(l) and Vapours(g) is also *one component system* because the composition of each phase can be expressed in terms of one constituent viz. sulphur.

(iii) Decomposition of  $\text{CaCO}_3$  by heat can be expressed according to the equilibrium



Thus there are three different constituents forming three different phases. But the composition of each phase can be expressed in terms of any two of the constituents. For example,

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

Phase	Composition
$\text{CaCO}_3$	$\text{CaO} + \text{CO}_2$
$\text{CaO}$	$\text{CaO} + 0 \text{CO}_2$
$\text{CO}_2$	$0 \text{CaO} + \text{CO}_2$

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

Phase	Composition
$\text{CaCO}_3$	$\text{CaCO}_3 + 0 \text{CO}_2$
$\text{CaO}$	$\text{CaCO}_3 - \text{CO}_2$
$\text{CO}_2$	$0 \text{CaCO}_3 + \text{CO}_2$

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

Phase	Composition
$\text{CaCO}_3$	$\text{CaCO}_3 + 0 \text{ CaO}$
$\text{CaO}$	$0 \text{ CaCO}_3 + \text{CaO}$
$\text{CO}_2$	$\text{CaCO}_3 - \text{CaO}$

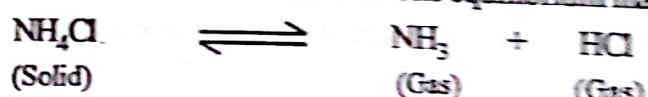
Thus in all the cases, the smallest number of constituents which fix the composition of the phases present at equilibrium is two and hence "dissociation of  $\text{CaCO}_3$  by heat" is a two component system.

(iv) Sodium sulphate-Water system. Such a system at equilibrium can include a number of phases like  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 7 \text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$  solution, ice, water and vapour, but the composition of each phase can be expressed by chemical equations, in terms of only anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) and water ( $\text{H}_2\text{O}$ ) as follows :

Phase	Composition
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4 + 10 \text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 \cdot 7 \text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4 + 7 \text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4$	$\text{Na}_2\text{SO}_4 + 0 \text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4$ Solution	$x \text{Na}_2\text{SO}_4 + y \text{H}_2\text{O}$
Ice	$0 \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
Water	$0 \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
Vapour	$0 \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

Thus the *smallest* number of independently variable constituents in terms of which the composition of the phases present at equilibrium can be expressed is two— $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . Hence it is also a *two component system*.

(v) Dissociation of ammonium chloride in a closed vessel. The equilibrium may be represented as



Thus there are three constituents —  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_3$  and  $\text{HCl}$  and two phases — one solid ( $\text{NH}_4\text{Cl}$ ) and one gaseous ( $\text{NH}_3 + \text{HCl}$ ).

So long as  $\text{NH}_3$  and  $\text{HCl}$  are present in equivalent amounts, the composition of each phase may be represented as  $\text{NH}_4\text{Cl}$ . Hence it is one component system. However, if an excess of  $\text{NH}_3$  or  $\text{HCl}$  is introduced, the composition of the gaseous phase can no longer be represented by  $\text{NH}_4\text{Cl}$  alone but one more component is required. Hence it becomes *two component system*.

In a chemically reactive system, the number of components is calculated as follows :

Number of components (C) = Total number of constituents or species, S (already present as well as produced as a result of reaction)  
 – Number of equations (E) representing equilibria between the constituents  
 – Number of restrictions (R) for electrical neutrality (if ions are considered)  
 or for material balance

Mathematically,  $C = S - E - R$

### PROBLEMS FOR PRACTICE

Calculate the number of components in

- (i) Solution of KCl in water
- (ii) Solution of acetic acid in water
- (iii) System containing  $\text{NaCl}(s)$ ,  $\text{Na}^+(aq)$ ,  $\text{Cl}^-(aq)$ ,  $\text{H}_2\text{O}(l)$ ,  $\text{H}_2\text{O}(g)$
- (iv) Dissociation of  $\text{PCl}_5(g)$ .

[Ans. (i) 2, (ii) 2, (iii) 3 and (iv) 2]

(3) Degree of freedom or Variance. The number of degrees of freedom or variance of a system is the smallest number of variable factors, i.e., temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the condition of the system may be completely defined.

Alternatively, the degrees of freedom of the system may be defined as the number of variable factors out of temperature, pressure and composition which can be varied without disturbing the number of phases present in equilibrium.

**Examples :** (i) **Ice-water-vapour system.** In this system, there are three phases of one component ( $\text{H}_2\text{O}$ ). These three phases can co-exist in equilibrium only at one particular temperature and under one particular pressure. Any variation of these factors will lead to the ultimate disappearance of one or more of the phases and, therefore, to the destruction of the system. Hence this system has no degree of freedom or in other words, it is invariant. The same result follows from Phase Rule i.e.,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

(ii) **Water-vapour system.** This system consists of two phases of one component. As the vapour pressure of water is definite at a definite temperature independent of the amount of water present, it follows that if the temperature is fixed, the vapour pressure is also fixed and conversely, fixing the pressure fixes the temperature. Thus the system has only one degree of freedom or in other words, it is univariant. The same result is obtained from Phase Rule i.e.,

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

(iii) **For a gas.** The temperature, pressure and concentration (volume) are related according to the equation  $PV = RT$ . Thus in order that the system may be completely defined, any two factors out of  $P$ ,  $V$  and  $T$  must be fixed. Hence it follows that a gas has two degrees of freedom or it is bivariant. Phase rule also leads to the same result i.e.,

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

**(4) Equilibrium.** A system is said to be in equilibrium if the properties like temperature, composition etc. of the various phases do not undergo any change with time. These equilibria may be two types, namely **true equilibrium** and **metastable equilibrium**.

A system is said to be in a state of true equilibrium if the same state can be achieved by approach from either direction. For example, the equilibrium between ice and water at 1 atm. pressure and  $0^\circ\text{C}$  is a true equilibrium because it can be attained by partial melting of ice or by partial freezing of water.

On the other hand, a state of a system which can be attained only from one direction and that too by very careful change of conditions is called a state of metastable equilibrium. For example, water at  $-2^\circ\text{C}$  can be had only by very careful cooling of liquid water but not by melting of ice. Hence water at  $-2^\circ\text{C}$  is said to be a state of metastable equilibrium. Such a state can be preserved only if no shock, stirring or 'seeding by the solid substance (ice)' takes place. In case any of these takes place, solidification sets in and the temperature rises to  $0^\circ\text{C}$ .

### 5.3. CRITERIA FOR PHASE EQUILIBRIA FOR MULTI-COMPONENT SYSTEM

As already discussed in Chapter 3, in order that equilibrium may exist among the different phases, the following three conditions must be satisfied. In other words, the following three equilibria must exist :

composition diagram. The diagrams so obtained giving the conditions of equilibria between various phases of a system are called phase diagrams or equilibrium diagrams. These diagrams contain a number of lines, areas and points of intersection, the significance of each of which has been discussed in the subsequent sections under the study of different systems.

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## ONE-COMPONENT SYSTEMS

### 5.7. APPLICATION OF PHASE RULE TO ONE-COMPONENT SYSTEMS

From the phase rule equation,  $F = C - P + 2$ , it is quite clear that when there is one component existing in one phase, i.e. when  $C = 1$  and  $P = 1$ , the maximum value for the degrees of freedom ( $F$ ) =  $1 - 1 + 2 = 2$ . Hence all systems of one component can be completely described graphically by stating two variable factors i.e. pressure and temperature on appropriate axes. From equational statement of phase rule, in systems of one-component, it will be observed that

(i) When the number of phases is reduced to one, the systems will have two degrees of freedom and are known as **Bivariant systems**.

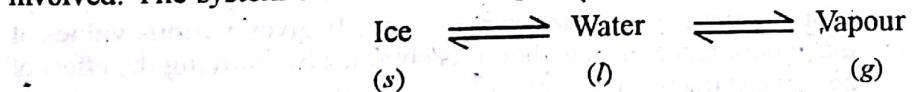
(ii) When the number of phases is two, the systems will possess one degree of freedom and are known as **Univariant systems**.

(iii) When the three phases co-exist, systems will possess no degree of freedom and are known as **Non-varient systems**.

In phase diagram of one component systems, bivariant systems are represented by 'areas', univariant systems by 'lines' and a non-varient system by a 'point'.

### 5.8. THE WATER SYSTEM

This is the most common example of the one component system as  $H_2O$  is the only chemical compound involved. The system consists of three phases.



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

(i) Liquid  $\rightleftharpoons$  Vapour

(ii) Solid  $\rightleftharpoons$  Vapour

(iii) Solid  $\rightleftharpoons$  Liquid

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

The number of phases that can exist in equilibrium at any point depends upon the conditions of temperature and pressure. These conditions have been determined experimentally and a phase diagram is obtained by plotting pressure against temperature (Fig. 5.3.). The phase diagram consists of :

(i) Three stable curve  $OA$ ,  $OB$ ,  $OC$  and one metastable curve  $OA'$

(ii) Three areas

(iii) Definite point,  $O$ .

#### L Curves

(i)  $OA$ . This is the vapour-pressure curve of water, representing the equilibrium between liquid water and vapour at different temperature. At any point on the curve, the two phases present are liquid water and water vapour. The curve starts from the point  $O$ , the freezing point of water and ends at  $A$ , the critical temperature ( $374^\circ\text{C}$ ) beyond which the two phases merge into each other. Consider any point on the curve. Now for a fixed

value of pressure, temperature has also a fixed value. Hence if by keeping the pressure constant, an attempt is made to raise the temperature then the vapour phase will disappear and if the temperature is lowered then the liquid phase will disappear. Therefore, to define the system completely at any time, it is necessary to mention temperature or pressure. In other words pressure being fixed, it is not necessary to mention temperature ; it is automatically fixed. Thus water-vapour system is univariant. It also follows from the phase rule equation,

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

(ii)  $OA'$ . The dotted curve  $OA'$ , a continuation of curve  $OA$  represents the vapour-pressure curve of supercooled water. It is a metastable curve. On slight disturbance, the supercooled phase at once changes to solid ice and curve merges into  $OB$ .

Two facts should be clearly noticed here :

- (a) There is no break in the vapour-pressure curve as the solid phase does not separate.
- (b) The vapour-pressure of the supercooled water, which is an unstable phase, is greater than that of solid (ice) which is the stable phase at that temperature.

(iii)  $OB$ . It is the sublimation curve or the vapour pressure curve of ice. It gives various values of temperatures and pressures at which ice and vapour can exist together. It is obtained by studying the effect of pressure on the freezing point of water. The curve starts from the point  $O$ , the freezing point of water and ends at  $B$  ( $-273^{\circ}\text{C}$ ). As temperature decreases, the vapour-pressure of ice tends to become insignificant. Again we see that for a particular temperature, there can be one and only one pressure value and vice versa. In other words, ice-vapour system is univariant.

(iv)  $OC$ . It is the melting point curve of ice and represents the equilibrium between ice and liquid water at various pressures. In other words, it shows the effect of pressure on the melting point of ice. It should be noted that the line  $OC$  is inclined towards the pressure axis. The slope of the curve  $OC$  clearly indicates that melting point of ice is lowered by increase of pressure. This fact is in agreement with the Clausius-Clapeyron equation. There is, however, no limit for the curve  $OC$ . It goes up to a point corresponding to 2240 atmospheres and  $-22^{\circ}\text{C}$ . At this point, one type of ice changes into another solid modification but the solid-liquid equilibrium still remains.

At any point on the curve  $OC$ , two phases (ice and liquid water) are present in equilibrium. Hence the system is univariant, i.e., degree of freedom is one.

**II. Areas.** The areas, i.e., the regions bounded by two lines give the conditions of temperature and pressure under which the single phase i.e., ice or liquid water or vapour is capable of stable existence. In area  $AOB$ , we have water vapour, in area  $BOC$ , we have ice and in area  $COA$ , we have liquid water. These areas are bivariant as to locate any point in the areas, temperature as well as pressure must be fixed, thus indicating two degrees of freedom. This also follows from phase rule equation

$$F = C - P + 2$$

$$F = 1 - 1 + 2 = 2$$

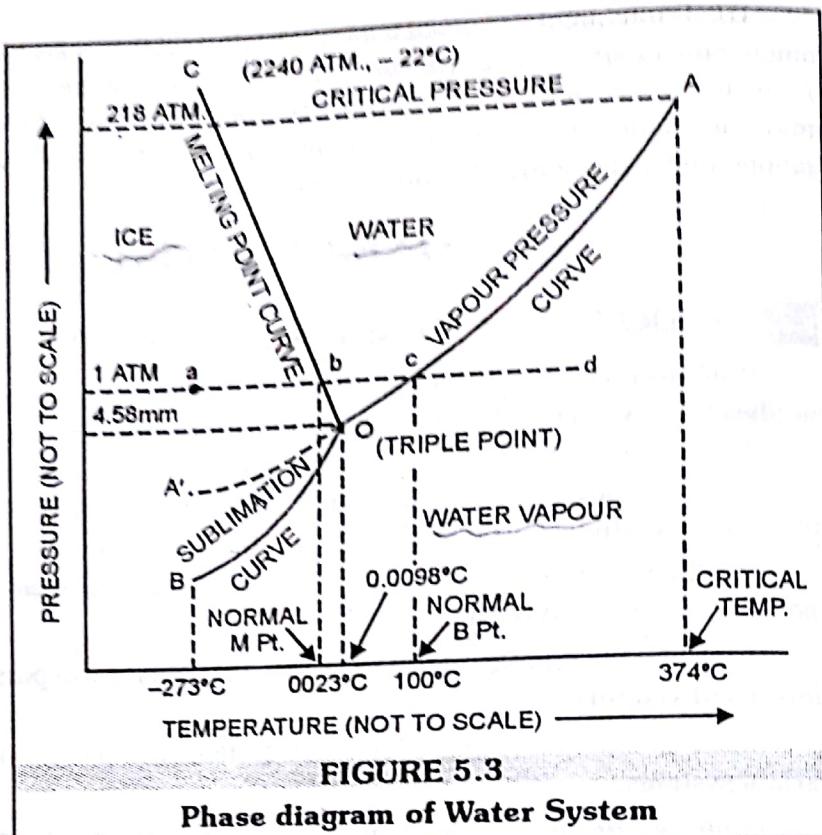


FIGURE 5.3

Phase diagram of Water System

**III Triple point.** It is a point where the three curves  $OA$ ,  $OB$ ,  $OC$  meet. At this point, the three phases—ice, water and vapour are in equilibrium. It should be noted that it is only a point, indicating that there is only one set of conditions under which it is possible for the three phases to exist together. The point  $O$  is a well-defined point corresponding to definite temperature of  $0.0098^{\circ}\text{C}$  and a definite pressure of  $4.58\text{ mm}$ . If either pressure or temperature is changed, then one of the three phases will disappear. Since on changing either pressure or temperature, one of the phases disappears therefore, the system at the point  $O$  has no degree of freedom. i.e., it is invariant. This also follows from phase rule equation

$$F = C - P + 2$$

$$\therefore F = 1 - 3 + 2 = 0$$

Summing up from the above discussion, the main features of the phase diagram of water system are tabulated below :

TABLE 5.1. Water System.

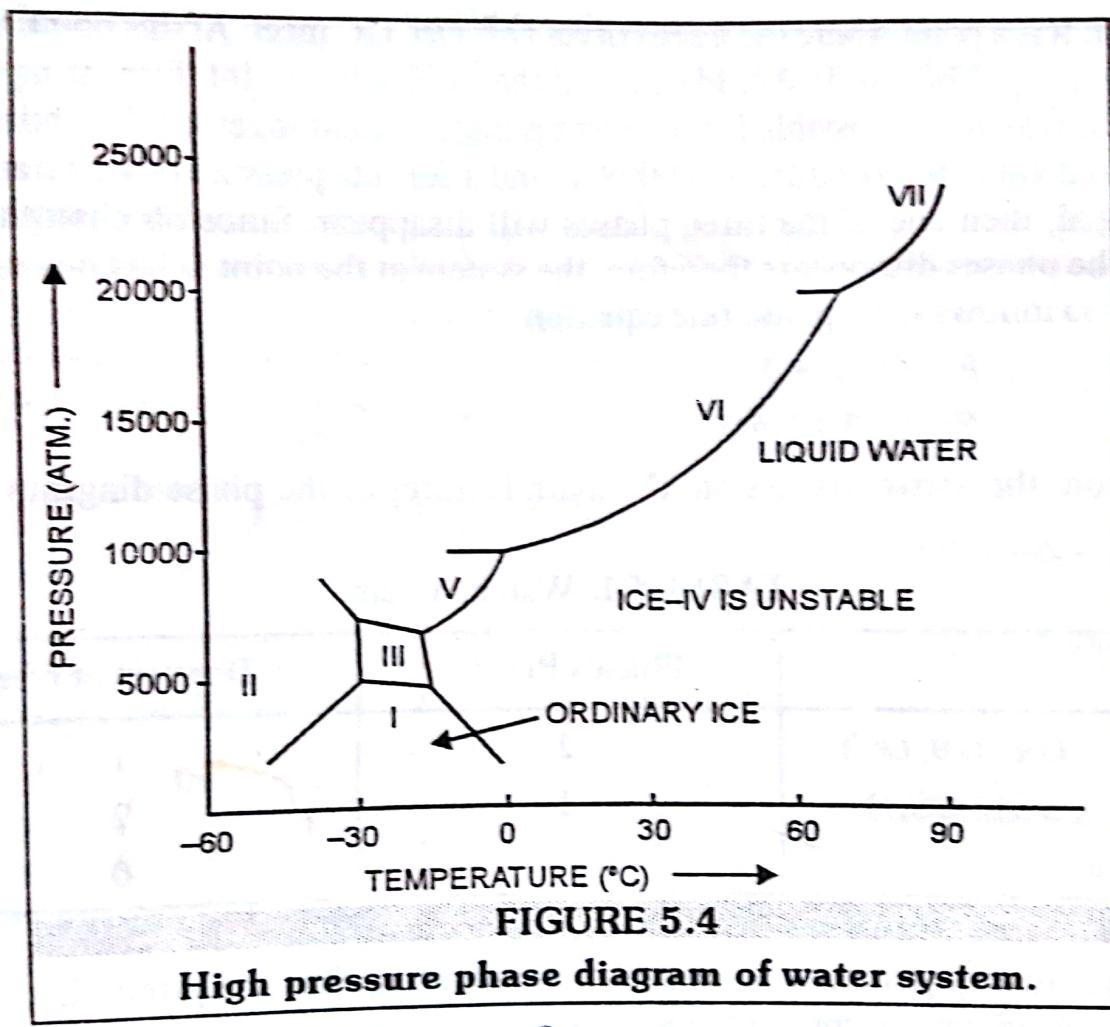
System	Phases Present	Degrees of freedom
Curves ( $OA$ , $OA'$ , $OB$ , $OC$ )	2	1
Areas ( $AOB$ , $BOC$ , $COA$ )	1	2
Triple Point $O$	3	0

**Effect of Change of Temperature at Constant Pressure on Water System.** Let us study the effect of temperature on the water system at a constant pressure of one atmosphere. Suppose we start with the conditions corresponding the point 'a' where water exists as ice at a temperature much lower than  $0^{\circ}\text{C}$  and then heat it slowly along the path  $abcd$  keeping pressure constant at one atmosphere. At the point 'a', the system is bivariant. When we reach the point 'b', melting of ice starts. Now there are two phases present (ice and liquid water), the system becomes univariant (i.e., has only one degree of freedom). Now the heat supplied simply helps more ice to melt but the temperature remains constant corresponding to point 'b' till whole of ice has melted. On further heating, the path  $bc$  is followed i.e., there is only liquid water (where  $P = 1$  so that  $F = 2$ ) whose temperature keeps on rising upto point  $c$ . At the point  $c$ , the heat supplied is used to convert the liquid water into vapour (so that  $P = 2$  and  $F = 1$ ) but temperature remains constant till the whole of the liquid water has changed into vapour. Beyond point  $c$ , heat supplied simply raises the temperature of the vapour along the path  $cd$  (where  $P = 1$  so that  $F = 2$ ).

In a similar manner, the effect of change of pressure at constant temperature on the water system can be studied.

**High Pressure Phase Diagram of Water System.** As already explained in the phase diagram of water system, the melting point of ice decreases with increase of pressure till it reaches a value of  $-22^{\circ}\text{C}$  at a pressure of 2240 atmosphere. The question arises what happens if pressure is further increased. It is observed that different forms of ice are formed which differ in density, crystal structure and certain other physical properties. The form of ice existing at 2240 atm with melting point of  $-22^{\circ}\text{C}$  is the ordinary ice and is called ice-I.

The forms or modifications obtained on increasing the pressure further are called ice-II, ice-III and so on upto ice-VII. The form ice-IV is unstable and its existence has not been confirmed. It is interesting to observe that melting points of these forms keep on increasing. The highest pressure form, ice-VII melts at about  $100^{\circ}\text{C}$  to form water at the pressure of 25,000 atmosphere. In fact, it is found that ice-VII is stable upto  $190^{\circ}\text{C}$  at a pressure of 40,000 atm. Thus imagine that the melting of ice can be so hot. The high pressure phase diagram of water system is shown in Fig. 5.4. Thus there are five more triple points in addition to the one already shown in Fig. 5.3.



**FIGURE 5.4**

**High pressure phase diagram of water system.**

## **CARBON DIOXIDE SYSTEM**

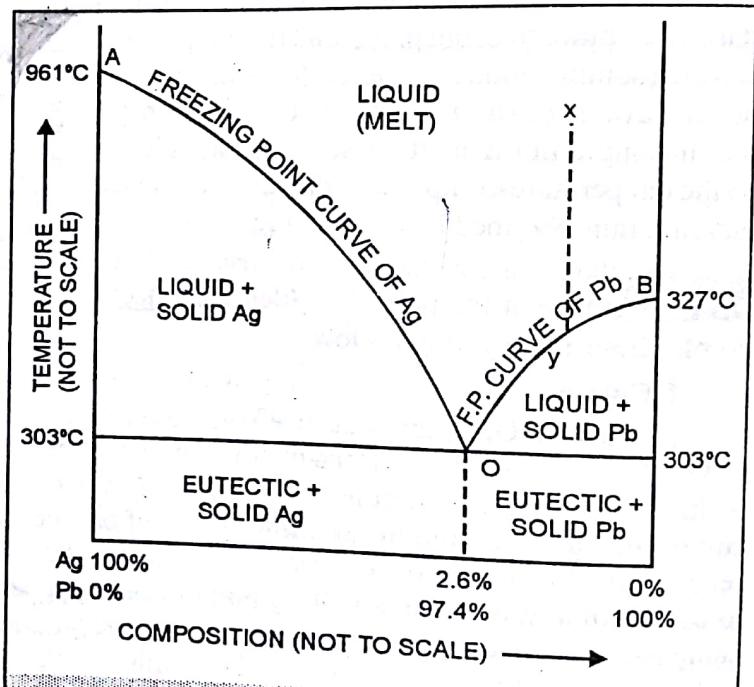
proportion in which they were present in the liquid phase. The temperature corresponding to the eutectic point  $O$  is called the **eutectic temperature**. This is always lower than the melting points of the components constituting the eutectic mixture. For example, in this system, eutectic mixture (containing about 40% Cd and 60% Bi by weight) melts at  $144^{\circ}\text{C}$ , a temperature lower than the melting point of bismuth ( $271^{\circ}\text{C}$ ) and that of cadmium ( $321^{\circ}\text{C}$ ).

### **5.16. LEAD-SILVER SYSTEM**

It is a two-component system consisting of the two components *lead* and *silver*. The various phases possible are (i) solid lead (ii) solid silver (iii) solution of lead and silver in the molten state (as they are completely miscible) and (iv) vapour.

Since small changes of pressure have negligible effect on the equilibrium existing between lead and silver in the solid state or in the molten state, so we can use the *reduced phase rule equation*,  $F' = C - P + 1$ . According to this equation, when  $F' = 0$ ,  $P$  will be 3. Thus the maximum number of phases (other than vapour) that can coexist would be three.

The phase diagram of lead-silver system is shown in the Fig. 5.15. The diagram is drawn taking temperature and composition along the axes. The equilibrium diagram consists of two curves  $OA$  and  $OB$ , intersecting at the point  $O$ .



**FIGURE 5.15**  
**Phase diagram of Lead—Silver system.**

### L Curves:

(i) **Curve OA.** It represents the *freezing point curve of silver* to which successive small quantities of lead are added. The point *A* indicates the melting point of pure silver ( $961^{\circ}\text{C}$ ). It is observed that the melting point of silver is lowered gradually by the addition of lead into it. All along this curve, the added lead goes into the solution and the separation of silver occurs till the point *O* is reached. At this point, no more lead goes into the solution, as the solution becomes saturated with respect to lead and hence the melting point of silver does not fall any longer. Thus the point *O* represents the lowest possible temperature ( $303^{\circ}\text{C}$ ) in the system that corresponds to fixed composition, viz., 2.6% Ag and 97.4% Pb. The point *O* is called the Eutectic point.

All along the curve *AO*, two phases—solid silver and liquid (melt) are present in equilibrium neglecting the vapour phase. Therefore the system is univariant as shown below :

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

(ii) **Curve BO.** It represents the *freezing point curve of lead* to which successive small amounts of silver are added. The point *B* represents the melting point of pure lead ( $327^{\circ}\text{C}$ ). It is seen that the addition of silver to lead lowers the melting point of lead. All along this curve, the silver which is added goes into the solution while the separation of lead takes place. This state of affairs continues till the point *O* is reached. At this point, no more silver goes into the solution and the solution is said to have become saturated with respect to silver. Hence the melting point of lead does not fall any longer.

All along this curve, two phases—solid lead and liquid melt are present in equilibrium. Therefore, as before,  $F' = C - P + 1 = 2 - 2 + 1 = 1$ , i.e., the system is univariant.

**II. Eutectic point, O.** This is the point where two curves *AO* and *BO* meet. At this point, solid lead, solid silver are in equilibrium with the fused mass, i.e., three phases are present. Therefore, there are no degrees of freedom, as according to *reduced phase rule equation*.

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

$$= 2 - 3 + 1 = 0$$

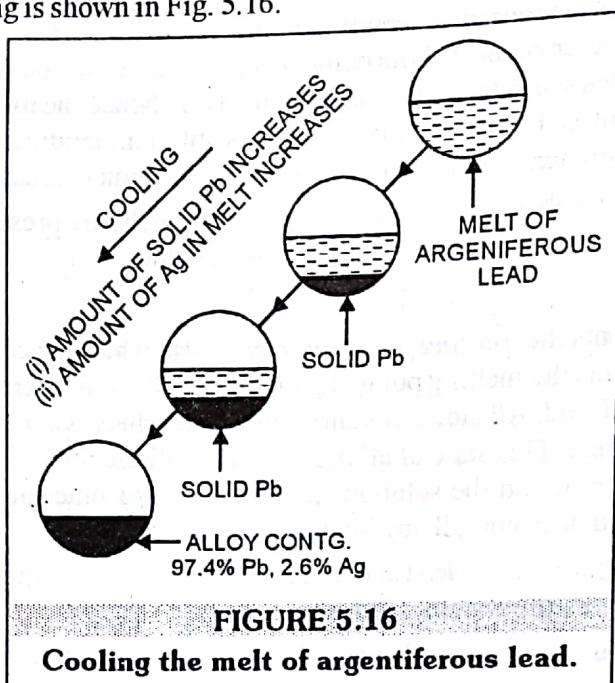
The point *O* represents the lowest possible temperature ( $303^{\circ}\text{C}$ ) below which a liquid phase cannot exist and above which the liquid phase cannot be enriched in either component by freezing out the other component. Such a liquid mixture of two components—Ag and Pb, which has the lowest freezing point compared to all other liquid mixtures is called eutectic mixture. (Greek; *eutectic* means easily melting). This mixture freezes out completely at a constant temperature and on freezing gives the two components as solid phases in the same proportion in which they are present in the liquid phase. The temperature corresponding to the eutectic point *O* is called the eutectic temperature. This is always lower than the melting point of the components constituting the eutectic mixture. For example, in the above system, we see that the alloy containing 2.6% silver and 97.4% lead melts at  $303^{\circ}\text{C}$ , a temperature lower than the melting point of Ag ( $961^{\circ}\text{C}$ ) and that of Pb ( $327^{\circ}\text{C}$ ).

### 5.17. PATTINSON'S PROCESS FOR THE DESILVERISATION OF LEAD

Galena (PbS, an ore of lead) is usually associated with silver. When galena is worked out for the extraction of lead, some traces of silver pass into it, because silver is soluble in lead to some extent. The lead thus obtained is known as argentiferous lead. The desilverisation of lead can be easily understood from the phase diagram of lead-silver system (shown in Fig. 5.15).

The argentiferous lead containing small percentage of silver is first of all heated to a temperature well above its melting point so that the system consists only of liquid phase represented by the point *x* in the figure. It is then allowed to cool gradually along the line *xy* without any change in concentration till the point *y* is reached. As soon as this point is attained, lead starts separating and solution will contain respectively increasing amounts of silver. Further cooling will shift the system along the line *yO*. Lead continues to separate out (which can be removed with the help of ladles/perforated spoons) and the melt continues to be richer and richer in silver, till the point *O* is reached where an alloy containing about 2.6% of silver is obtained.

The above principle is employed in Pattinson's process which is used for increasing the relative proportions of silver in the alloy. The relative increase in the amount of solid lead that separates out and in the proportion of silver in the melt on cooling is shown in Fig. 5.16.



**FIGURE 5.16**  
**Cooling the melt of argentiferous lead.**

**TABLE 5.3. Some Eutectic Systems**

Components with m.pt. (°C)		Eutectic temp. (°C)	% of A in Eutectic mixture
A	B		
Ag (961°)	Pb (327°)	303°	2.6% Ag
Zn (419°)	Cd (321°)	270°	67% Zn
Bi (271°)	Cd (321°)	140°	60% Bi
Ag (961°)	Cu (1083°)	778°	71.8% Ag
Au (1064°)	Ti (302°)	131°	27% Au

### 5.18. POTASSIUM IODIDE-WATER SYSTEM

This is another example of a two-component system in which the two components are KI and H<sub>2</sub>O in terms of which the composition of every phase can be expressed. Since KI does not form hydrates, the only phases that are possible are (i) solid KI, (ii) ice, (iii) solution of KI in water and (iv) vapour. Thus this system is similar to lead-silver system. However, there is one important difference in the fact that whereas lead (m.pt. = 327°C) can exist at the melting point of silver (*viz.* 961°C), water, being volatile, cannot exist at the melting point of KI (which is very high). Thus we cannot reach the melting point of KI in presence of water and hence this curve is incomplete.

Neglecting the vapour phase as before (because the small changes of pressure have negligible effect on the equilibrium)\*, the system becomes a *condensed system* and the *reduced phase rule equation* can be applied. Thus the experimentally observed values of temperatures can be plotted against composition to give a *t-c* diagram as shown in Fig. 5.17. The diagram consists of the curves AO, BO, the point O and the various

\* Vapour phase is neglected because the experiments are carried out at atmospheric pressure and the vapour pressure is negligible in comparison to the atmospheric pressure and the

areas above and below the curves  $AO$  and  $BO$ , as described below :

### L Curves :

(i) **Curve AO.** It represents the freezing point curve of water to which successive quantities of potassium iodide are added or in other words, the curve  $AO$  shows the effect of the addition of potassium iodide on the freezing point of water. The point  $A$  represents the freezing point of water (or m. pt. of ice) under normal conditions. At this point, three phases—ice, liquid water and vapour are in equilibrium. It is observed that by the gradual addition of potassium iodide to it, the freezing point of water is lowered and curve  $AO$  slants downwards. This, however, does not go on indefinitely, for, as soon as the solution is saturated with respect to potassium iodide, the lowest temperature is reached at the point  $O$ ; then further addition of KI will not produce further lowering in the freezing point of water. The point  $O$  corresponds to a concentration of 52% potassium iodide and represents the lowest temperature that can be attained in this system.

This eutectic temperature in this case is called **Cryohydric point** and the eutectic itself is called a **Cryohydrate**, reminding us of the separation of ice as a solid phase.

All along the curve  $AO$ , two phases, namely solution and ice are in equilibrium (neglecting the vapour phase). Therefore the system is univariant as

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

(ii) **Curve OB.** It is the solubility curve of potassium iodide in water at different temperatures. It represents the effect of temperature on the solubility of solid potassium iodide. It is observed that solubility of potassium iodide increases with the rise of temperature and is maximum at the point  $B$ , the boiling point of the saturated solution. However, the curve comes to an end before it can touch the 100% potassium iodide axis. Conversely, if the saturated solution of potassium iodide in water is cooled, potassium iodide separates out and the solution becomes dilute and the curve  $BO$  is followed till the point  $O$  is reached. Here the solution freezes as a whole with a fixed composition.

All along the curve  $OB$ , there are two phases—solid KI and solution in equilibrium, and being a two-component system, the number of degrees of freedom according to reduced phase rule equation would be

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

**II. Cryohydric point, O.** It is the point where the two curves  $AO$  and  $BO$  intersect. Here, three phases—ice, solid salt and solution are in equilibrium. If the vapour phase is not neglected, then the fourth phase is also present. Point  $O$  is therefore called a *quadruple point*. If we apply the phase rule, we find that the system is invariant, i.e.

$$F = C - P + 2 = 2 - 4 + 2 = 0$$

Therefore, any change in temperature or composition will cause one of the phases to disappear. The point  $O$  corresponds to a definite temperature ( $-22^\circ\text{C}$ ) and composition (52% KI and 48% ice).

**III. Areas.** The area above  $AOB$  represents only the unsaturated solution phase. In the region  $AOC$ , two phases, viz., solid ice and saturated solution are in equilibrium whereas in the region  $BOD$  the two phases in equilibrium are solid KI and saturated solution. The system below the eutectic line  $COD$  is entirely solid, containing excess of ice to the left of the point  $O$  and excess of solid KI to the right of the point  $O$ .

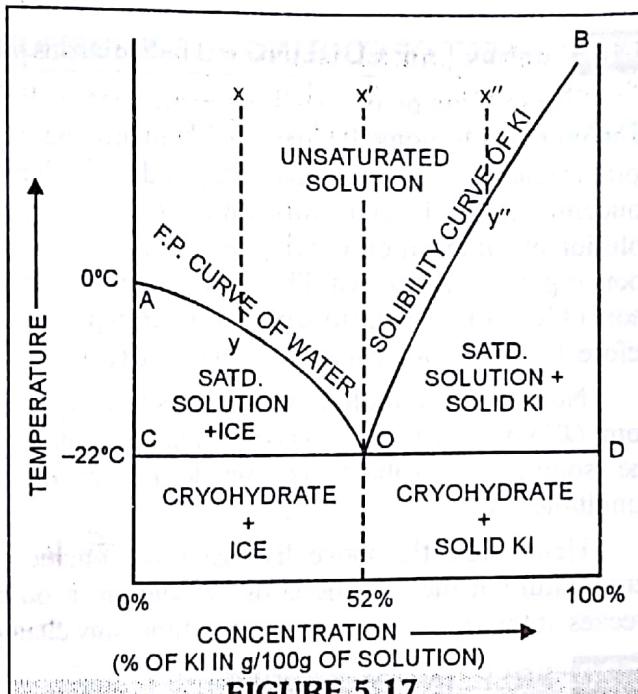


FIGURE 5.17

Phase diagram of KI-H<sub>2</sub>O system.

### 5.19. EFFECT OF COOLING POTASSIUM IODIDE SOLUTION

The solution phase exists in the area above  $AOB$ . Let the solution represented by the point  $x$  be allowed to cool gradually along the line  $xy$  without any change in composition till the point  $y$  is reached. As soon as this point is reached, ice starts separating, and on further cooling, solution will continue becoming more and more concentrated till the cryohydric point  $O$  is reached where solid KI also makes its appearance. Similarly, if a solution of composition  $x''$  lying on the right hand of the point  $O$  is cooled then KI will begin to separate as soon as point  $y'$  is reached. The composition will, therefore, change with temperature along  $y''O$  and more and more of KI will continue to separate out until point  $O$  is reached (here ice also begins to deposit). Ultimately, as before, the whole of the mixture will freeze to give eutectic mixture.

Now consider a solution of composition represented by the point  $x'$  lying vertically above the cryohydric point  $O$ . When such a solution is allowed to cool gradually along the line  $x'O$  without any change in composition, the solution will solidify as a whole, i.e., on reaching the point  $O$ , both ice and KI start separating out simultaneously.

Hence from the above discussion we conclude that all solutions on cooling show no further change in temperature at the eutectic point  $O$ . Moreover, on cooling a solution of eutectic composition, the solution freezes at the eutectic temperature without any change in composition.

### 5.20. FREEZING MIXTURES

Addition of a salt to ice results in the melting of some ice and a lowering of temperature. Mixtures of ice and salts are thus frequently used for getting low temperature and such mixtures in general are called *freezing mixtures*. A good freezing mixture is one which satisfies the following conditions :

(i) *It should have a low cryohydric temperature.* This condition is fulfilled by having a salt which is highly soluble.

(ii) *The heat of solution of the salt should be high.* This is generally true of salts, solubility of which rapidly increases on increasing the temperature.

(iii) *The components should be such that an intimate mixture can be obtained from them.*

(iv) *The material should be cheap.*

In actual practice, the common freezing mixture is made from ice and common salt (sodium chloride). Although the common salt is very cheap, it is not good salt to use because the heat of solution of this salt is very low and the heat absorbed is almost due to the heat of fusion of ice. The calcium chloride hexa-hydrate and ice form a good freezing mixture because this has a low cryohydric point and high heat of solution. Some common and important freezing mixtures are given below :

TABLE 5.4. Freezing Mixtures

First Component	Parts by wt.	Second Component	Parts by wt.	Lowest Temperature
$\text{NH}_4\text{Cl}$	1	Ice	4	-15.4°C
$\text{NaCl}$	33	Ice	100	-21°C
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	10	Ice	7	-55°C
$\text{NaNO}_3$	1	Ice	2	-17.8°C
Alcohol	...	Solid $\text{CO}_2$ (Dry ice)	...	-72°C
Ether	...	Solid $\text{CO}_2$ (Dry ice)	...	-77°C
Acetone	...	Solid $\text{CO}_2$ (Dry ice)	...	-70°C

For attaining very low temperatures, (-50 to -70°C), acetone-dry ice mixture is quite often used. Acetone is taken in a Dewar or insulated flask and dry ice is added to it till the lowest temperature is attained.