

8

PHASE EQUILIBRIA

8.1 INTRODUCTION

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state.

Thus we speak of solid, liquid and gas phases of a substance

e.g. solid phase of H_2O = Ice,

liquid phase of H_2O = water

and gas phase of H_2O = steam

and of various solid phases of a substance (e.g. white and black allotropes of phosphorus).

In this chapter phase rule given by Gibbs will be discussed with help of phase diagram. Phase diagram is a map of temperature and pressure. Phase diagram of a substance shows the regions of pressure and temperature at which different phases are thermodynamically stable. The lines separating the regions, which are called phase boundaries, show the values of P and T at which two phases coexist in equilibrium.

The practical importance of the expressions, we derive is that they show how the vapour pressure of a substance varies with temperature and how the melting point varies with pressure. One of the most impressive way of presenting the physical changes of state that a substance can undergo is in terms of its phase diagram. Spontaneous conversion of one phase into another is called phase transition. It occurs at characteristic temperature for a given pressure. Thus at 1 atm, ice is stable phase of water below $0^\circ C$, but above $0^\circ C$ liquid water is more stable. That means below $0^\circ C$, Gibbs energy decreases as liquid water changes into ice and above $0^\circ C$, the Gibbs energy decreases as ice changes into liquid water. The temperature at which phase transition takes place is called transition temperature at which the two phases are in equilibrium and Gibbs energy is minimized at that pressure. Sometimes a transition which appears to be thermodynamically stable is kinetically hindered, so does not take place e.g. change of diamond into graphite at normal temp. and pressure is thermodynamically stable because molar Gibbs energy of the graphite is low under above mentioned conditions. But this is kinetically slow/hindered process because for the change (diamond graphite) C atoms will have to change their locations. This is a slow process at normal temp. and pressure. So the attainment of this type of change is kinetically hindered. Thermodynamically unstable phases that persist (e.g. diamond in above discussed case) because their transitions are kinetically hindered and are called Metastable phase.

8.2 PHASE RULE

J.W. Gibbs deduced the phase rule, which is a general relationship between the variance (degree of freedom) F, the number of components C and number of phases at equilibrium P, for a system of any composition. It is represented mathematically as

$$F = C - P + 2$$

8.3 DIFFERENT TERMS

Phase

~~It is defined as any part of a system which is uniform throughout in chemical composition and physical state, mechanically separable from other parts of system i.e. physically and chemically different from other parts of the system.~~

Table 8.1 Different Types of Phases in different systems

System	Phases
1. Mixture of gases which do not react	1 Phase
2. Ice	1 Phase
3. Ice & water	2 Phases
4. Ice, Water, Vapours	3 Phases
5. 2 miscible different liquids	1 Phase
6. 2 immiscible liquids	2 Phases
7. 2 Miscible different solids	2 Phases
8. Solid naphthalene and its vapours	2 Phases
9. Alloy of 2 metals (if the metals are immiscible)	2 Phases
10. Alloy of 2 Metals (If the metals are miscible)	1 Phase
11. 2 Allotropes	2 Phases

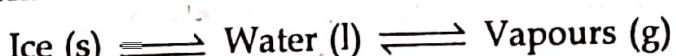
It is not always easy to decide whether a system consists of one phase or two phases.

Components

~~Any substance present in a system~~ It is defined as minimum number of independent species necessary to define the composition of all the phases present in the system at equilibrium.

The term component should be carefully distinguished from constituents, when a chemical species (an ion, or molecule) that is present.

Example. Water system

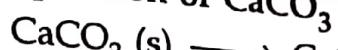


One component system because composition of each of three phases can be directly expressed as H_2O . In this system H and O are not the components. Because these are not independently variable but are in a fixed ratio (2 : 1)

Example. Sulphur system.

It has 4 phases :- Monoclinic (s), Rhombic (s), liquid (l) and vapours (g).
It is a one component system because composition of each phase can be expressed in terms of one constituent S.

Example. Decomposition of CaCO_3



This is a 3 phase system, but no. of components = 2. Because composition of each phase can be expressed by 2 constituents.

(a) If the two components are CaO and CO_2

Phase	Composition
CaCO_3	$\text{CaO} + \text{CO}_2$
CaO	$1\text{CaO} + 0\text{CO}_2$
CO_2	$0\text{CaO} + 1\text{CO}_2$

(b) If the constituents are CaCO_3 and CO_2

Phase	Composition
CaCO_3	$1\text{CaCO}_3 + 0\text{CO}_2$
CaO	$\text{CaCO}_3 - \text{CO}_2$
CO_2	$0\text{CaCO}_3 + 1\text{CO}_2$

(c) If the constituents are CaCO_3 and CaO

Phase	Composition
CaCO_3	$1\text{CaCO}_3 + 0\text{CaO}$
CaO	$0\text{CaCO}_3 + 1\text{CaO}$
CO_2	$\text{CaCO}_3 - \text{CaO}$

So any two components can expresss the composition of all the three phases present in the system.

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 condition of system may be completely defined.

Examples. Ice-water-vapour system. The three phases can coexist in equilibrium only at one particular temperature and at one particular pressure is called triple point ~~pressure~~. Any variation of these factors will lead to disappearance of one or more phases. Hence this point has no degree of freedom $F = 0$. It is invariant point. Triple point is not in our control i.e. for triple point to exist, one particular temperature and one particular pressure is required i.e. 0.0098°C and 4.578 atm . So no variable. With variation in temp., vapour pressure will also change. But for triple point any temperature value other than 0.0098°C is not

valid. With variation of pressure, temperature will change. But for triple point any pressure value other than 4.578 atm is not valid. So $F = 0$ for triple point.

Example. Water vapour system.

As V.P. of water is definite at definite temperature independent of the amount of water.

So if temp. is fixed, V.P. gets automatically fixed. And by fixing pressure, the temperature gets fixed automatically. Here $F = 1$ univariant. It can be explained further as, "even by changing the temperature or V.P. along the water vapour curve, water-vapour equilibrium will keep on existing" i.e. one variable either temperature or pressure can be arbitrarily fixed.

Boiling Point and Critical Point

The temperature at which the vapour pressure of a liquid is equal to external pressure is called boiling temperature at that pressure.

Boiling does not occur when a liquid is heated in a closed vessel. Instead the vapour pressure and hence density of vapour increases but density of liquid decreases continuously with increase in temp. A stage comes when density of two phases is equal and surface between two phases disappears. The temp. at which the surface disappears is called Critical Temperature.

The vapour pressure at critical temp. is called Critical Pressure. *The point of intersection of critical Temp. and critical P is called critical point*

Melting Point and Triple Point

The temp. at which under a specific pressure, the liquid and solid phases of a substance coexist in equilibrium is called melting temperature. A substance melts at the same temp. at which it freezes, the melting temperature of a substance is the same as freezing temperature.

There is a set of conditions under which three different phases of a substance coexist in equilibrium. These conditions are represented by Triple point, a point at which three boundaries meet. The triple point of a substance occurs at a single definite temperature and pressure. The triple point of water lies at 0.0098°C and 4.578 atm and three phases of water coexist in equilibrium at no other combination of P and T. The triple point is invariant ($F = 0$).

Importance of Phase Rule

1. This rule is very useful to calculate number of components, number of phases and degrees of freedom for various equilibrium states of the system.
2. Phase rule is applicable to physical as well as chemical equilibria irrespective of nature or amounts of the substances.
3. This rule is very useful in heterogeneous systems and metallurgy. It gives us information about the complex formation among different components.

8.4 HOW THE PHASE DIAGRAM IS PLOTTED

The data for the construction of phase diagram is determined experimentally by a variety of methods :

- (i) Thermal analysis
- (ii) Metallographic method
- (iii) X-ray diffraction.

All the methods have their own advantages and limitations but the X-ray diffraction method is simple, precise and useful. This method measures lattice dimensions and indicates the appearance of new phase either by change in lattice dimensions or by appearance of a new crystal structure.

This information collected is plotted between T and P along right axis and a phase diagram is resulted. *called P-T diagram and is used for one component system.* If phase diag. is plotted between Temp (T) and composition (C), it is called T-C diag & is used for two/multi component system.

8.5 ONE COMPONENT SYSTEM

When there is one component and one phase in a system i.e. when $C = 1, P = 1, F = 1$, $C - P + 2 = 1 - 1 + 2 = 2$. Hence all systems of one component can be described graphically, by stating two variable factors i.e. pressure (P) and temperature (T) on appropriate axis.

For a one component system

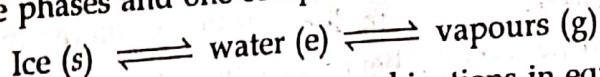
- (i) If $P = 1, F = 2 \Rightarrow$ Bivariant system
- (ii) If $P = 2, F = 0 \Rightarrow$ Non-variant system

In phase diagram of one component system, bivariant systems are represented by areas, univariant systems are represented by lines and non-variant systems by points.

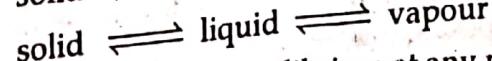
8.5.1 Few Examples of One Component System

The water system

This system has three phases and one component. It is represented as



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



The number of phases that can exist in equilibrium at any point depend on temperature and pressure conditions. The conditions have been determined experimentally and phase diagram is obtained by plotting temperature against pressure.

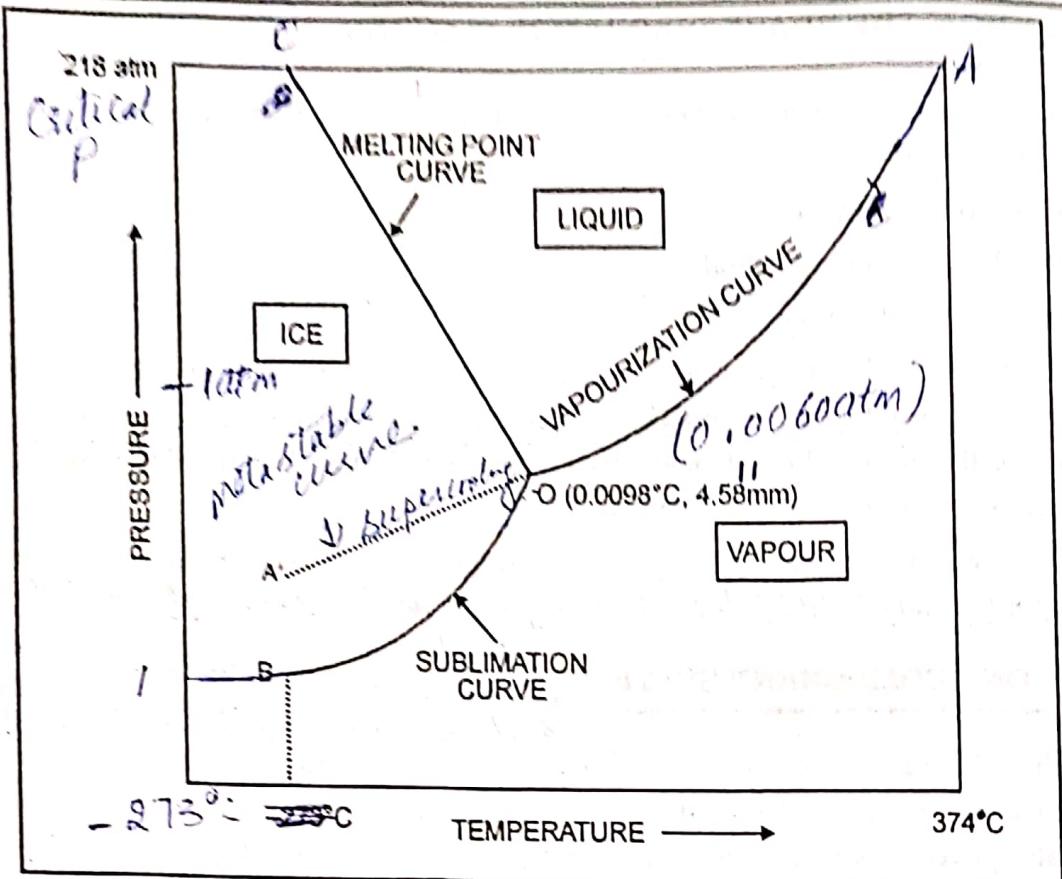


Fig. 8.1 Phase diagram of Water System

- It has :
- (1) Three stable curves and one metastable curve
 - (2) Three areas
 - (3) Point O

Curves / Lines.

Curve OA. It is vapourization curve. It starts from O and ends at A. On this curve liquid \rightleftharpoons water vapours lies at different temperature. Point A is called critical pt. As critical temp. is 374°C. and critical Pressure is 218 atm. For this curve, $F = C - P + 2, 1 - 2 + 2 = 1$ i.e. curve is univariant. Beyond A, two phases merge into each other.

On any point of this curve, for fixed value of P, T is automatically fixed. (By keeping P constant, if an attempt is made to increase the T, then vapour phase will disappear and if is lowered, liquid phase will disappear). To define the system at any point it is necessary to mention either T or P i.e. $F = 1$. *i.e. To stay on this line T & P can't be changed independently*

Curve OA'. Metastable curve i.e. extention of OA. It is vapour pressure curve of super cooled water. On this curve, at all the points, there exists equilibrium of super-cooled water (below 0°C) \rightleftharpoons vapours. It is metastable curve. Any variation in temp./ pressure results into submerging of this curve into OB.

This is a univariant curve.

There are two facts :

(a) As long as solid phase does not separate, there is no break in vapour pressure curve.

(b) The vapour pressure by super-cooled water (unstable phase) is greater than solid form of water i.e. ice (stable phase).

2. Curve OB. It is sublimation curve. On every point of this curve there exists solid \rightleftharpoons vapours. The vapour pressure of solid ice $<$ vapour pressure of super-cooled water. It starts with O and ends up at B (-273°C). For a particular temperature, value of P gets fixed and vice versa i.e. system is univariant, $F = 1$.

3. Curve OC. It is melting point curve, it starts with O and ends at C (2000 atm, and -20°C). Beyond this one type of ice changes into other solid. At every point on this curve, there exist ice \rightleftharpoons water equilibrium. It can be seen that line OC is inclined towards pressure axis. The slope of line indicates that melting point of ice gets lowered by increasing pressure. It is a univariant curve i.e. $F = 1$.

Areas. This system has three areas :

Area AOB is a Bivariant area.

$$F = C - P + 2$$

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

In the area AOB vapour phase is represented.

Area AOC. In this area we have liquid water. It is bivariant area ($F = 2$).

Area BOC. In this area solid water is present. It is a bivariant area ($F = 2$).

Triple point. At this point, the three phases are in equilibrium, i.e. three curve OA, OB, OC meet at this point.

Neither T nor P can be changed.

$$F = C - P + 2$$

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

The point 'O' is non-variant point. If either T or P is changed, one of the phase will disappear. The point O corresponds to temp. of 0.0098°C and 4.58 mm pressure.

Metastable Equilibrium

Sometimes water can be cooled below its freezing point (0°C) without formation of ice.

A state of system which can be attained only from one direction and that too by careful change of conditions is called state of metastable equilibrium, e.g. at -2°C water can be had (called super-cooled water) by careful cooling of water below 0°C and not by melting ice below 0°C . Hence water at -2°C is said to be in state of metastable equilibrium. Such a state can be prescribed only if no disturbance like shock, stirring or seeding by solid (ice) takes place. Super-cooled water can be kept as such almost indefinitely if presence of ice is carefully avoided. But as soon as a small particle of ice is brought into contact with super-cooled water, entire water freezes.

Metastable state has higher vapour pressure than stable one.

On OA the supercooled water \rightleftharpoons Vapour, equilibrium exists.

from each other at low temperature.

8.6 TWO COMPONENT SYSTEMS

A system in which composition of all the phases can be expressed by two components is called two component system. For this

$$F = C - P + 2$$

Two component system has maximum three degrees of freedom as $C = 2$ always.

So, If

$$P = 1 \text{ (minimum) so}$$

$$F = 2 - 1 + 2 = 3 \text{ i.e. trivariant}$$

For any other value of P , $F < 3$

If $P = 2$, $F = 2 - 2 + 2 = 2$ i.e. bivariant

If $P = 3$, $F = 2 - 3 + 2 = 1$ i.e. univariant

If $P = 4$, $2 - 4 + 2 = 0$ i.e. non-variant.

Three degrees of freedom means three variables i.e. temp., pressure and concentration.

In most of the cases, pressure is kept const. at atmospheric value and temp. concentration graph i.e. phase diagram is drawn. A phase diagram at const. value of temp. is called Isothermal.

A phase diagram at const. value of composition is called Isoplethal diagram.

Condensed systems. If a system (for example an alloy, It has no gas phase) has only solid and liquid phases, then a slight change in pressure will have very little effect on the system. In such systems vapourisation is not considered and pressure is kept constant. Such systems are called condensed systems. In these systems the degree of freedom is reduced by one. So reduced phase rule for condensed system is :

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

F' = degrees of freedom possessed by a system in addition to pressure.

Two Component System having Solid-Liquid Equilibria

Two component systems of this type are of 2 types :

Type I. Those in which two components do not react with each other but simply mix into each other in the molten state or in solution e.g. lead-silver system and $KI - H_2O$ system.

Eutectic system. It is defined as a binary system of type I of two substances which are miscible in all the proportions in the liquid (molten) phase but do not react chemically. They have the property of lowering each others' freezing point. The min. freezing point attained is called Eutectic point and composition corresponding to Eutectic point is called Eutectic mixture. This type of system is called Eutectic system. Hence solid solution of such a 2 components system which has lowest freezing point at all the possible mixtures of the components is called Eutectic.

Eutectic means easy to melt.

Eutectic pt. is an invariant point. Eutectic is not a compound because

(i) Components are not present in the stoichiometric proportion.

When Eutectic was seen under microscope both the components of Eutectic was seen to lie as separate crystals. (ii) Their physical properties such as density were almost equal to the mean value of their constituents. Hence Eutectic is a mixture and not a compound.

Difference between Mixture and Compound (Recap only)

Mixture	Compound
(1) Constituents of mixture may be present in any ratio.	(1) Constituents should be present in a fixed ratio by mass.
(2) Properties of mixture are mean of their components properties.	(2) Properties of compound are entirely different from its components.

Type II. Those in which two components react with each other resulting into formation of a compound.

Two component system of type II are of 2 types :

(a) In which 2 pure components react to form a compound which is stable upto its M.Pt. This type of compound is called to have congruent melting point.

e.g. $\text{FeCl}_3 - \text{H}_2\text{O}$, hydrate formed has congruent M.Pt.

(b) In which 2 pure components react to form a compound which does not remain stable upto its melting point. When such a compound is heated, it starts decomposing before its melting point to give a new solid phase and a solution. This is called transition or peritectic reaction shown as (where C_1 is new compound of one pure constituent formed below M.Pt. of C_2) $C_2 \rightleftharpoons C_1 + \text{solution (melt)}$.

(Where C_2 is compound formed with incongruent M.Pt.). This type of compound is said to have incongruent melting pt. e.g. $\text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ system.

8.6.1 Significance of phase diagram of systems of Type-I

~~* Knowledge of temperature-composition diagrams for solid mixtures guides the design of important industrial processes such as manufacture of semiconductors and liquid crystal displays.~~

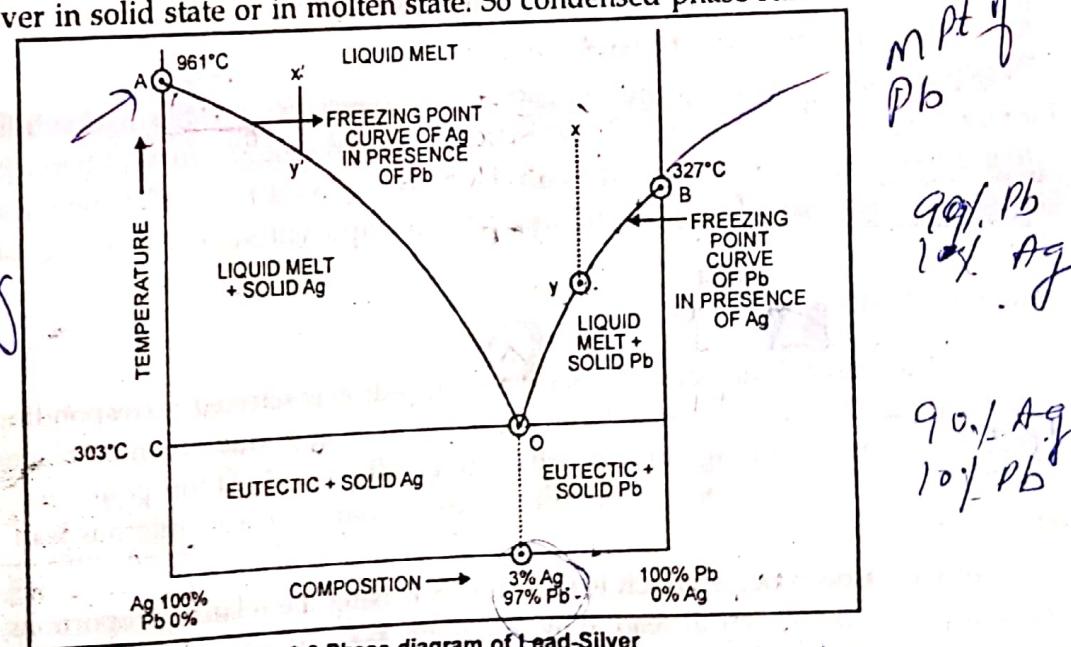
8.6.2 Some Examples of two component systems of Type-I

In this section we shall consider systems where solid and liquid phase may both be present at temperature below the boiling point.

1. Lead-Silver system

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

Since small change in the pressure has negligible effect on equilibrium existing between lead and silver in solid state or in molten state. So condensed phase rule is used.



Legnit
mix solid Ag & lead

Now let us discuss it :

Curve OA. It is called freezing point curve of Ag in the presence of Pb. Point A represents 100% Ag and is melting point of Ag i.e. 961°C . On addition of small amount of lead to pure Ag at its melting point, lead forms a fused mass with molten silver, and small amount of solid Ag separates out. This process continues till the point O (i.e. M.Pt. of Ag is reduced gradually on addition of lead in to it). At O point a saturated solution of Pb is formed with molten silver which corresponds to 3% Ag and 97% Pb. At this point no more lead goes into silver solution so melting point of silver does not fall any more. Point O corresponds to temp. 303°C . Point O is called Eutectic point. All along AO, two phases i.e. solid silver and liquid melt are present in equilibrium with each other so

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

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

i.e. Univariant curve

Curve OB. It is freezing point curve of lead in the presence of Ag. It starts from B i.e. melting point of lead 327°C . On addition of Ag to molten lead, it forms the solution and solid Pb separates out. This continues till the point O is reached. This means melting point of lead is lowered, on addition of Ag. At point O a saturated solution of 3% Ag and 97% Pb is formed. So no more Ag goes into solution. So M. Pt. of Pb does not fall any more.

All along this curve solid Pb and liquid melt are present in equilibrium

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

So this curve is univariant.

Eutectic point O. This point corresponds to temperature 303°C and composition 3% Ag and 97% of Pb. At this point solid Ag, solid Pb and liquid melt are in equilibrium.

i.e.

$$P = 3; C = 2$$

$$F = C - P + 1$$

$$= 2 - 3 + 1 = \text{zero.}$$

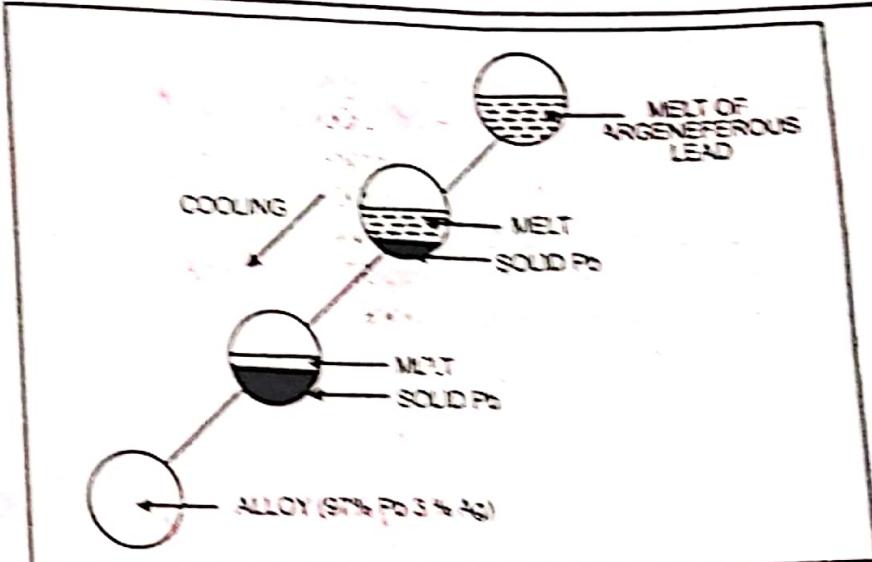
So point O is non-variant point.

On lowering the temperature below 0, melt disappears and whole mass solidifies while increase in temperature beyond 303°C melts the solid. Liquid mixture of two components Ag and Pb, which has the lowest freezing point compared to all other liquid mixture is called Eutectic mixture. Above discussed two component system is an e.g. of Eutectic system.

Effect of Cooling

x point represents the liquid phase. If a composition is selected corresponding point x, if it is cooled along line xy i.e. without changing the composition then on reaching point y, lead will start separating out and will continue till point O. At this point only 3% of Ag is left. This technique is very useful for (1) desilverisation of argentiferous lead. (i.e. lead having Ag.).

(2) In Pattinson process which is used for increasing the relative proportions of silver in the melt i.e. Argentiferous lead alloy (i.e. along X'Y')



On cooling, amount of solid lead increases, and amount of Ag in melt increases.

2. Potassium iodide-water system. This is another example of a two-component system in which the two components KI and H₂O can express all the phases of the system, which are : (i) solid KI (ii) solid water i.e. ice (iii) solution of KI in water and (iv) vapour.

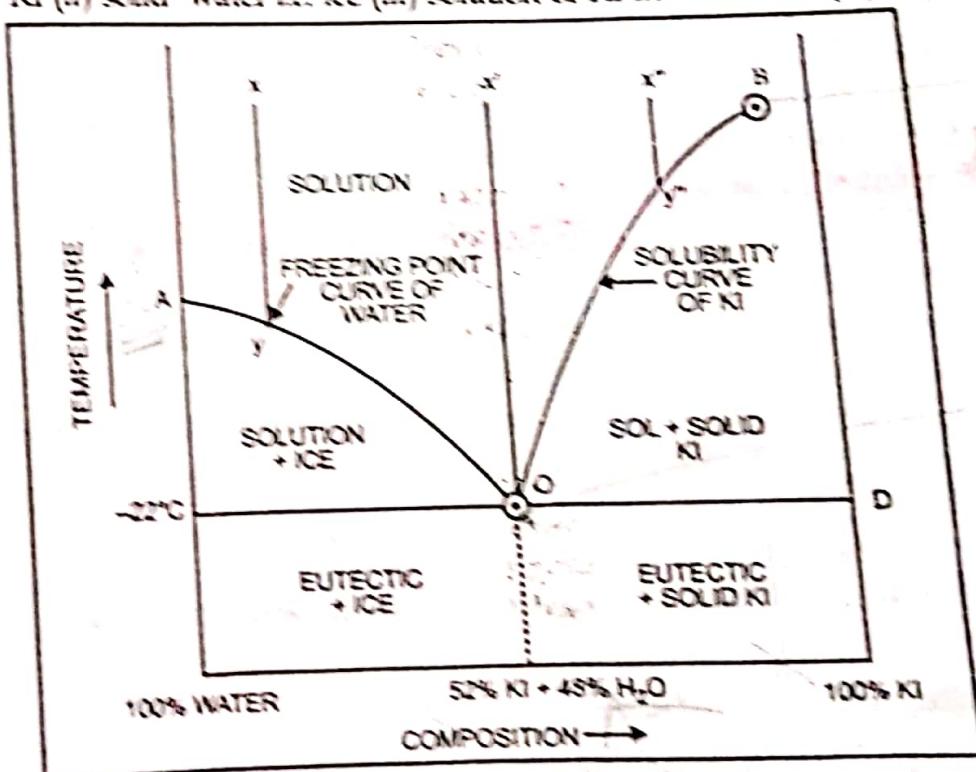


Fig. 8.7 Phase diagram of KI-H₂O

This system is similar to lead-silver system. But one main difference is that lead can exist at melting point of silver, but water cannot exist at melting point of KI. (Because water gets evaporated as melting point of KI is very high). We cannot reach the melting point of KI in presence of water. So this curve is incomplete.

This is a condensed system.

Curve OA. This is freezing point curve of water or melting point curve of ice. It represents freezing point of water 0°C and 100% water. This curve represents that freezing point of water decreases with addition of KI to it upto point O, i.e. on addition of KI to water, solid water i.e. ice separates out and KI goes into water to form solution. So at this curve solid ice and solution are in equilibrium i.e. 2 phases, so $P' = C = P + 1$

$= 2 - 2 + 1 = 1$ i.e. Univariant curve. Corresponding to O temperature is $\sim 22^{\circ}\text{C}$ and composition is 52% KI. The point O is called cryohydric point.

Curve OB. It is solubility curve of KI starting from O. Solubility of KI increases in water on increasing the temperature and solubility is max. at point B.

Point B is B. Pt. of saturated solution of KI in water. In other words the curve OB can be explained as : On cooling the saturated solution of the KI, it separates out and the solution becomes dilute. This process continues till point O is reached.

All along the curve OB two phases are there; solid KI and solution, so $P' = 1$ i.e. univariant curve.

Eutectic point in this case is called cryohydric point and Eutectic is called cryohydric. Mixtures of KI and ice formed at eutectic point was at one time considered to be a definite compound of the form of salt hydrate. This was given name cryohydrate. But later on it was realised that (1) physical properties of the composition and eutectic point is equal to mean value of the two components (2) Under microscope the solid showed 2 types of separate crystals. (These are two properties of a mixture and not of compound).

Hence, it was decided that is composition at point O, a mixture is not a compound.

Cryohydric point 'O'. It is point of intersection of OA and OB. At this point, solid ice, solid KI and solution exist in equilibrium.

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

i.e. Non-varient point

Point O corresponds to temperature $\sim 22^{\circ}\text{C}$ and fixed composition of 52% KI and 48% water.

Below the cryohydric temperature solution disappears and whole of the mass solidifies.

Areas. (i) Area above AOB represents unsaturated solution phase.

(ii) AOC area represents solid ice and solution.

(iii) Area BOP represents solid KI and solution.

(iv) Area below line COD has solid phases i.e. excess of ice on left side and excess of KI on right side.

Effect of cooling on KI solution

Area above AOB shows solution. If any point x is selected, this corresponds to a solution of fixed composition. If this solution is cooled without varying the composition then on reaching the point y , ice will start separating out till the point O is reached, where solid KI also appears. Likewise if a solution of composition x'' is cooled without changing its composition i.e. along the line $x''y''$, on reaching the pt. y'' , solid KI will start separating out i.e. solution will start becoming dilute and will continue along $y''O$ curve till point O where solid ice also appears.

Now if a solution of composition x' is cooled along $x' O$ then on reaching point O ice and solid KI will appear simultaneously.

It can be concluded that all the solutions on cooling show no change, in composition at eutectic point O. On cooling a solution of eutectic composition, freezes without any change in composition.

Significance of KI-H₂O System. If sufficient amount of KI (say 52%) has been added, the temperature will fall upto cryohydric point i.e. - 22°C. At this point, temperature remains constant.

8.6.3 Freezing Mixtures

If salt is added to ice, it will result into melting of ice and lowering of temperature and salt will go into water so formed. Mixtures of ice and salts are frequently used for getting the low temperatures. Such mixtures are called freezing mixtures. A good freezing mixture should have :

- (i) low cryohydric point
- (ii) heat of solution of salt should be high (solubility of salt increases with increase in temperature).
- (iii) components should form an intimate mixture.
- (iv) the material used should be cheap.

In actual practice, common freezing mixture is made up of ice and NaCl. Although NaCl is cheap but heat of solution of this salt is very low.

Calcium Chloride-hexahydrate and ice forms a good freezing mixture because it has a high heat of solution and low cryohydric point.