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The Phase Rule

CHAPTER

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THE STATEMENT

The phase Rule is an important generalization dealing with the behaviour of heterogeneous systems. In general it may be said that with the application of *phase rule* it is possible to predict qualitatively by means of a diagram the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium. This relationship governing all heterogeneous equilibria was first discovered as early as 1874 by an American physicist Willard Gibbs. **Gibb's Phase Rule** is free from flaws and limitations which are a common feature of all other generalizations of Physical Chemistry based on hypothetical assumptions as to the nature of the constitution of matter. It may be stated mathematically as follows :

$$F = C - P + 2$$

where F is the number of *degrees of freedom*, C is the number of *components* and P is the number of *phases* of the system. The terms 'phase', 'component', and 'degree of freedom' involved in the statement of the Phase Rule have a special significance and a clear understanding of these terms is essential before we proceed further with the subject.

WHAT IS MEANT BY A 'PHASE' ?

A phase may be defined as : **any homogeneous part of a system having all physical and chemical properties the same throughout.** A system may consist of one phase or more than one phases.

- (1) A system containing only liquid water is **one-phase** or **1-phase system** ($P = 1$)
- (2) A system containing liquid water and water vapour (a gas) is a **two-phase** or **2-phase system** ($P = 2$).
- (3) A system containing liquid water, water vapour and solid ice is a **three-phase** or **3-phase system**.

A system consisting of one phase only is called a **homogeneous system**.

A system consisting of two or more phases is called a **heterogeneous system**.

Explanation of the Term 'Phase'

Ordinarily three states of matter-gas, liquid, and solid are known as phases. However in *phase rule*, a **uniform part of a system in equilibrium is termed a 'phase'**. Thus a liquid or a solid mixture could have two or more phases.

Let us consider a few examples to understand the meaning of the term phase as encountered in phase rule.

(1) **Pure substances.** A pure substance (solid, liquid, or gas) made of one chemical species only, is considered as one phase. Thus oxygen (O_2), benzene (C_6H_6), and ice (H_2O) are all 1-phase systems. *It must be remembered that a phase may or may not be continuous.* Thus, whether ice is present in one block or many pieces, it is considered one phase.

(2) **Mixtures of gases.** All gases mix freely to form homogeneous mixtures. Therefore any mixture of gases, say O_2 and N_2 , is a 1-phase system.

(3) **Miscible liquids.** Two completely miscible liquids yield a uniform solution. Thus a solution of ethanol and water is a 1-phase system.

(4) **Non-miscible liquids.** A mixture of two non-miscible liquids on standing forms two separate layers. Hence a mixture of chloroform ($CHCl_3$) and water constitutes a 2-phase system.

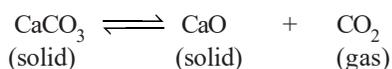
(5) **Aqueous solutions.** An aqueous solution of a solid substance such as sodium chloride (or sugar) is uniform throughout. Therefore it is a 1-phase system.

However, a saturated solution of sodium chloride in contact with excess solid sodium chloride is a 2-phase system.

(6) **Mixtures of solids.** (i) By definition, a **phase must have throughout the same physical and chemical properties.** Ordinary sulphur as it occurs in nature is a mixture of monoclinic and rhombic sulphur. These allotropes of sulphur consist of the same chemical species but differ in physical properties. Thus mixture of two allotropes is a 2-phase system.

(ii) **A mixture of two or more chemical substances contains as many phases.** Each of these substances having different physical and chemical properties makes a separate phase. Thus a mixture of calcium carbonate ($CaCO_3$) and calcium oxide (CaO) constitutes two phases.

Let us consider the equilibrium system : the **Decomposition of Calcium carbonate**. When calcium carbonate is heated in a closed vessel, we have



There are two solid phases and one gas phase. Hence it is a 3-phase system.

WHAT IS MEANT BY 'COMPONENTS'?

A system ' C ' in the *Phase Rule equation* stands for the number of components of a system in equilibrium. The term component may be defined as : **the least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation.**

Explanation of the Term 'Component'

To understand the above definition and to use it for finding the number of components of a system, remember that :

- The chemical formula representing the composition of a phase is written on LHS.
- The rest of the chemical constituents existing independently in the system as represented by chemical formulas are placed on RHS.
- The quantities of constituents on RHS can be made minus (-) or zero (0) to get at the composition of the phase on LHS.

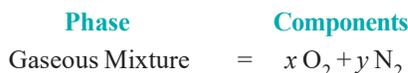
Now let us proceed to discuss the number of components of some systems.

(1) **Water and sulphur systems are 1-component systems.** Water system has three phases : *ice*, *water*, and *water vapour*. The composition of all the three phases is expressed in terms of one chemical individual H_2O . Thus water system has one component only.

Sulphur system has four phases : rhombic sulphur, monoclinic sulphur, liquid sulphur and sulphur vapour. The composition of all these phases can be expressed by one chemical individual sulphur (S). Hence it is a 1-component system.

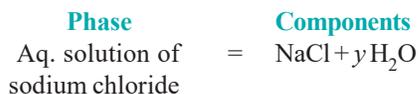
As is clear from above, when all the phases of a system can be expressed in terms of one chemical individual, it is designated as a one-component or 1-component system.

(2) **Mixture of gases.** A mixture of gases, say O_2 and N_2 , constitutes one phase only. Its composition can be expressed by two chemical substances O_2 and N_2 .



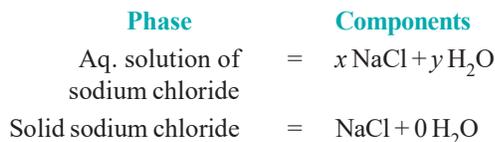
Hence a mixture of O_2 and N_2 has two components. In general the number of components of a gaseous mixture is given by the number of individual gases present.

(3) **Sodium chloride solution.** A solution of sodium chloride in water is a 1-phase system. Its composition ($xNaCl.yH_2O$) can be expressed in terms of two chemical individuals, sodium chloride and water.



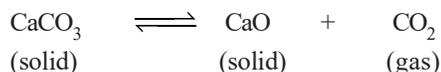
Therefore an aqueous solution of sodium chloride or any other solute is a two-component or 2-component system.

A saturated solution of sodium chloride, in contact with excess solid sodium chloride has two phase, namely aqueous solution and solid sodium chloride. The composition of both phase can be expressed in terms of two chemical individuals $NaCl$ and H_2O .



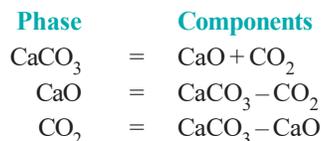
Hence a saturated solution of sodium chloride or any other solute in contact with solid solute, is 2-component system.

(4) **Decomposition of Calcium carbonate.** When calcium carbonate is heated in a closed vessel, the following equilibrium system results.

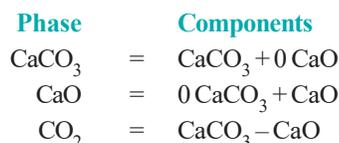


It has three phase : calcium carbonate, calcium oxide, and carbon dioxide. The composition of all the phase can be expressed in terms of any two of the three chemical substances in equilibrium.

Let us select calcium oxide (CaO) and carbon dioxide (CO₂) as the components. Then we can write,



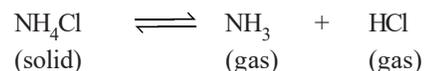
Again, selecting calcium carbonate (CaCO₃) and calcium oxide (CaO) as the components, we have



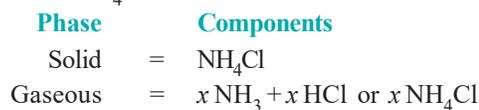
Thus decomposition of calcium carbonate is a 2-components system.

Furthermore, as is clear from the above examples, **by the components of a system is meant the number of chemical individuals and not any particular chemical substances by name.**

(5) **Dissociation of Ammonium chloride.** Ammonium chloride when heated in a closed vessel exists in equilibrium with the products of dissociation, ammonia (NH₃) and hydrogen chloride gas (HCl).



The system consists of two phase, namely, solid NH₄Cl and the gaseous mixture containing NH₃ and HCl. The constituents of the mixture are present in the same proportion in which they are combined in solid NH₄Cl. The composition of both the phase can, therefore, be expressed in terms of the same chemical individual NH₄Cl.



Thus dissociation of ammonium chloride is a one-component system.

DEGREES OF FREEDOM

The term **Degree of Freedom** represented by F in the phase Rule equation ($F = C - P + 2$) is defined as follows : **the least number of variable factors (concentration, pressure and temperature) which must be specified so that the remaining variables are fixed automatically and the system is completely defined**

A system with $F = 0$ is known as **nonvariant** or having no degree of freedom.

A system with $F = 1$ is known as **univariant** or having one degree of freedom.

A system with $F = 2$ is known as **bivariant** or having two degrees of freedom.

Explanation of the Term Degree of Freedom

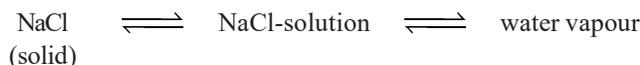
A system is defined completely when it retains the same state of equilibrium (or can be reproduced exactly) with the specified variables. Let us consider some examples.

(1) **For a pure gas, $F = 2$.** For a given sample of any pure gas $PV = RT$. If the values of pressure (P) and temperature (T) be specified, volume (V) can have only one definite value, or that the volume (the third variable) is fixed automatically. Any other sample of the gas under the same pressure and temperature as specified above, will be identical with the first one. Hence **a system containing a pure gas has two degrees of freedom ($F = 2$).**

(2) **For a mixture of gases, $F = 3$.** A system containing a mixture of two or more gases is completely defined when its composition, temperature and pressure are specified. If pressure and temperature only are specified, the third variable *i.e.*, composition could be varied. Since it is necessary to specify three variables to define the system completely, **a mixture of gases has three degrees of freedom ($F = 3$).**

(3) **For water \rightleftharpoons water vapour, $F = 1$.** The system water in equilibrium with water vapour, has two variables *temperature* and *pressure*. At a definite temperature the vapour pressure of water can have only one fixed value. Thus if one variable (temperature or pressure) is specified, the other is fixed automatically. Hence **the system water has one degree of freedom ($F = 1$).**

(4) **For saturated NaCl solution, $F = 1$.** The saturated solution of sodium chloride in equilibrium with solid sodium chloride and water vapour.



Thus the system is completely defined if we specify temperature only. The other two variables *i.e.*, the composition of NaCl-solution (solubility) and vapour pressure have a definite value at a fixed temperature. Hence **the system has one degree of freedom.**

(5) **For ice-water-vapour system, $F = 0$.** In the system $\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour}$, the three phases coexist at the freezing point of water. Since the freezing temperature of water has a fixed value, the vapour pressure of water has also a definite value. The system has two variables (temperature and pressure) and both these are already fixed. Thus the system is completely defined automatically, there being no need to specify any variable. Hence **it has no degree of freedom ($F = 0$).**

DERIVATION OF THE PHASE RULE

Consider a heterogeneous system in equilibrium of C components in which P phases are present. We have to determine the degrees of freedom of this system *i.e.*, the number of variables which must be arbitrarily fixed in order to define the system completely. Since the state of the system will depend upon the temperature and the pressure, these *two variables* are always there. The concentration variables, however, depend upon the number of phases. In order to define the composition of each phase it is necessary to specify the concentration of $(C - 1)$ constituents of each phase, the concentration of the remaining component being determined by difference. For P phases, therefore, the total number of concentration variables will be $P(C - 1)$ and these along with the two variables mentioned above *viz.*, temperature and pressure, make the total number of the variables of the system equal to $[P(C - 1) + 2]$.

On thermodynamic consideration when a system is in equilibrium, the partial molal free energy of each constituent of a phase is equal to the partial molal free energy of the same constituent in every other phase. Since the partial molal free energy of the constituents of a phase is a function of the temperature, pressure and $(C - 1)$ concentration variables, it follows that if there is one component in two phases, it is possible to write one equation amongst the variables and if there is one component in three phases, this fact may be written with the help of *two equations*. In general, therefore, when P phases are present, $(P - 1)$ equations are available for each component and for C components, the total number of equations or variables are $C(P - 1)$.

Since the number of equations is equal to the number of variables, the number of *unknown*

variables or degrees of freedom (F) will be :

$$\begin{aligned} F &= \text{No. of variables} - \text{Number of equations} \\ &= [P(C-1)+2] - [C(P-1)] \\ &= PC - P + 2 - PC + C \\ &= C - P + 2 \\ F &= C - P + 2 \end{aligned}$$

ONE-COMPONENT SYSTEM

For a one-component system we can write the phase rule equation as :

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

Three cases may arise :

Case 1. When only **one phase** is present,

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

Thus the system is **bivariant**. It can be completely defined by specifying the two variables, temperature and pressure. Or that, both the temperature and pressure can be varied independently. Therefore **a single phase is represented by an area on P, T-graph.**

Case 2. When **two phases** are in equilibrium,

$$F = 3 - 2 = 1$$

The system then has one degree of freedom and is termed **monovariant**. This means that the pressure cannot be changed independently if we change the temperature. The pressure is fixed automatically for a given temperature. **A two-phase system is depicted by a line on a P, T-graph.**

Case 3. When **three phases** are in equilibrium,

$$F = 3 - P = 3 - 3 = 0$$

$$\therefore F = 0$$

The system has zero degree of freedom and is termed **nonvariant or invariant**. This special condition can be attained at a definite temperature and pressure. The system is, therefore, defined completely and no further statement of external conditions is necessary. **A three-phase system is depicted by a point on the P, T-graph.** At this point the three phases (solid, liquid, vapour) are in equilibrium and, therefore, it is referred to as the **Triple point**.

PHASE DIAGRAMS

A phase diagram is a **plot showing the conditions of pressure and temperature under which two or more physical states can exist together in a state of dynamic equilibrium**. Fig. 19.1 is a typical phase diagram for a one-component system. The diagram consists of : (a) the Regions or Areas; (b) the Lines or Curves; and (c) the Triple point.

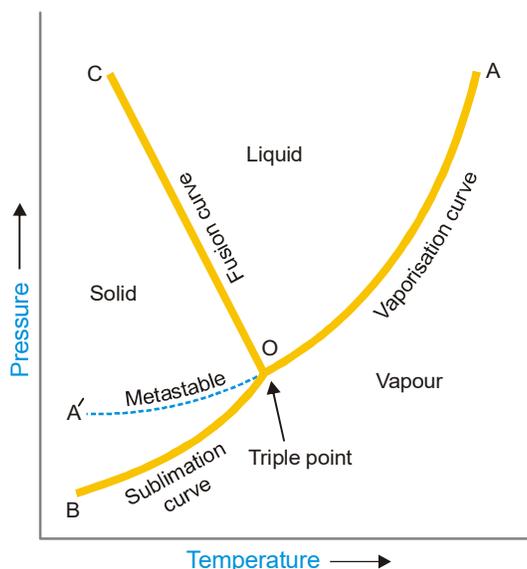
The significance of the characteristic features (Areas, Curves, Triple point) of a phase diagram are discussed below.

(1) Regions or Areas

The diagram is divided into three regions or areas which are labelled as 'solid', 'liquid', and 'vapour'. These areas in Fig. 19.1 are *COB*, *COA* and *AOB*. **Each of the three areas shows the conditions of temperature and pressure under which the respective phase can exist.** Applying the phase rule to the system when only one phase is present, we have

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

i.e., each single phase has two degrees of freedom.



■ **Figure 19.1**
A typical phase diagram of a one component system.

Thus **each area of phase diagram represents a bivariant system**. At conditions wholly within one of the three areas, both the variables (pressure and temperature) can be varied independently without causing a change in the state of equilibrium. Therefore in order to define the condition of the phase both pressure and temperature must be stated.

(2) Lines or Curves

There are three lines or curves separating the regions or areas. These **curves show the conditions of equilibrium between any two of the three phases** *i.e.*, solid/liquid, liquid/vapour, solid/vapour.

- Solid/liquid line (OC) which represents the equilibrium $Solid \rightleftharpoons Liquid$, is referred to as the **Melting curve** or **Fusion curve**.
- Liquid/vapour line (OA) which represents the equilibrium $Liquid \rightleftharpoons Vapour$, is referred to as the **Vapour Pressure curve** or **Vaporisation curve** for the liquid.
- Solid/vapour line (OB), which represents the equilibrium $Solid \rightleftharpoons Vapour$, is referred to as the **Sublimation curve**.

Applying phase rule to a one-component two-phase system.

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

Thus phase rule predicts that the two phase equilibria stated above will have one degree of freedom. Along any of three lines on the phase diagram when one variable (pressure or temperature) is specified, the other is fixed automatically.

(3) Triple Point

The *three* boundary lines enclosing the *three areas* on the phase diagram intersect at a common point called the *Triple point*. A **triple point shows the conditions under which all the three phases (solid, liquid, vapour) can coexist in equilibrium**. Thus the system at the triple point may be represented as :



Applying the phase rule equation, we have

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

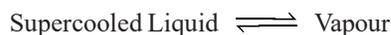
which predicts that the system has no degree of freedom.

At the triple point both pressure and temperature on the diagram are fixed and, therefore, the system is nonvariant. This implies that if we try to change temperature or pressure, the equilibrium will be disturbed. For example, if we lower the pressure on the system, all the liquid will vaporise, leaving only two phases.

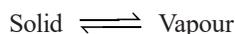
In case of water system, the temperature and pressure for the triple point are 0.0076° and 4.58 mm Hg respectively.

Metastable Equilibrium

The vapour pressure curve AO of the liquid phase terminates at O , when the liquid freezes (or solidifies). However by careful cooling of the liquid under conditions that crystals do not form, the curve AO can be extended to A' . This means that the liquid can be cooled far below the freezing point or 'supercooled' without separation of the crystals. The supercooled liquid is in an unstable condition. On the slightest disturbance as introduction of a seed crystal, the entire liquid solidifies rapidly. Thus the dashed curve OA' represents a **metastable equilibrium**,



This system at once reverts to the true stable system



under suitable conditions. It is noteworthy that the dashed curve of the metastable liquid lies above the normal sublimation curve (BO). This implies that **the vapour pressure of the metastable phase is always higher than that of the stable phase at the same temperature.**

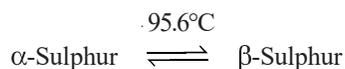
POLYMORPHISM

The occurrence of the same substance in more than one crystalline forms is known as Polymorphism. This phenomenon is shown by both elements and compounds. In the case of elements the term **allotropy** is often used. The individual crystalline forms of an element are referred to as **polymorphs** or **allotropes**. Rhombic and monoclinic sulphur are two polymorphs or allotropes of sulphur. The polymorphic or allotropic forms of an element have distinct physical properties and constitute separate phases.

Allotropy can be divided into three types : Enantiotropy, Monotropy and Dynamic allotropy.

(1) Enantiotropy

In some cases one polymorphic form (or allotrope) can change into another at a definite temperature when the two forms have a common vapour pressure. This temperature is known as the **transition temperature**. One form is stable above this temperature and the other form below it. **When the change of one form to the other at the transition temperature is reversible, the phenomenon is called enantiotropy and the polymorphic forms enantiotropes.** For example, rhombic sulphur (α -Sulphur) on heating changes to monoclinic sulphur (β -Sulphur) at 95.6°C (transition temperature). Also, monoclinic sulphur, on cooling, again changes to rhombic sulphur at 95.6°C . That is,



Thus α -Sulphur and β -Sulphur are enantiotropic.

(2) Monotropy

It occurs when one form is stable and the other metastable. **The metastable changes to the stable form at all temperatures and the change is not reversible.** Thus there is no transition temperature as the vapour pressures are never equal. This type of polymorphism is exhibited by phosphorus,



Another example is graphite and diamond, graphite being stable and diamond metastable, although the change is infinitely slow.

(3) Dynamic allotropy

Some substances have several forms which can coexist in equilibrium over a range of temperature. The amount of each is determined by the temperature. The separate forms usually have different molecular formulae but the same empirical formula. **This form of allotropy, known as dynamic allotropy, resembles enantiotropy in that it is reversible but there is no fixed transition point.**

An example of dynamic allotropy is provided by liquid sulphur which consists of three allotropes S_μ , S_π and S_λ .



These three forms of sulphur differ in molecular structure. S_λ is S_8 , S_π is S_4 while formula of S_μ is not known. The composition of the equilibrium mixture at 120°C and 444.6°C (b.p. of sulphur) is :

120°C	S_μ 0%	S_π 3.7%	S_λ 96.3%
444.6°C	S_μ 37%	S_π 4%	S_λ 59%

EXPERIMENTAL DETERMINATION OF TRANSITION POINT

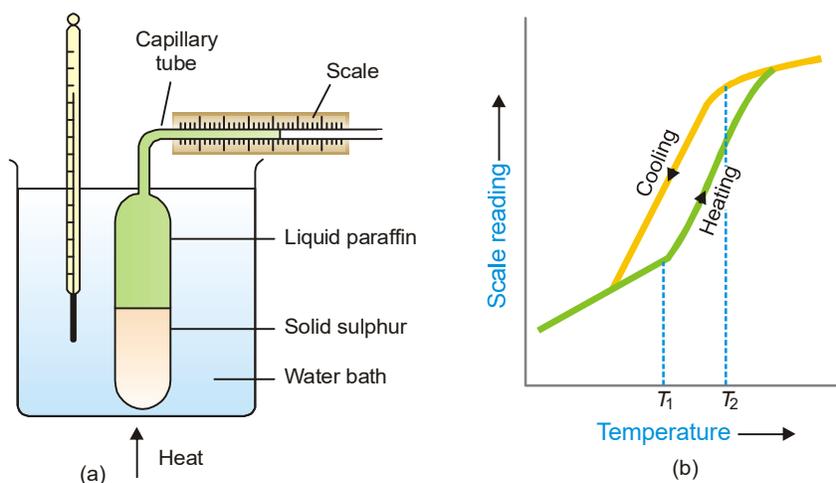
The temperature at which a polymorphic substance changes from one form to another, is known as the transition temperature or transition point. For example, rhombic variety of sulphur is converted to the monoclinic form of sulphur at 95.6°C at atmospheric pressure. The transition temperature in a particular case can be determined by measuring a change in physical properties such as colour, density, solubility, etc.

(1) Colour change

If a little mercury (II) iodide is placed in a melting point tube attached to a thermometer and heated in some form of apparatus (*e.g.*, electrical heater), it is possible to record temperature at which the red mercury (II) iodide changes to the yellow form.

(2) Density change

As rhombic sulphur changes to monoclinic sulphur, there is a decrease in density and, therefore, an increase in volume. The change in volume is employed to measure the transition temperature by using an apparatus known as **Dilatometer** shown in Fig. 19.2.



■ **Figure 19.2**
(a) A dilatometer; (b) Change in volume plotted against temperature recorded with a dilatometer.

Some powdered rhombic sulphur is placed in the glass bulb and liquid paraffin (an inert liquid) is introduced above the sulphur. The apparatus is then immersed in a heating water-bath, the temperature of which is raised. The scale reading and the temperature is recorded every minute. A plot of liquid level in the capillary against temperature gives a curve as in Fig. 19.2 (b). On cooling of the dilatometer, reverse changes take place but due to thermal lag the curve assumes the form shown in the figure. The transition temperature is taken as the mean of the respective temperatures where expansion starts (T_1) and contraction begins (T_2).

(3) Solubility change

Two forms of the same substance have different solubilities but at the transition point they have identical solubility. Thus if solubility-temperature graph is plotted for the two forms, it is found to consist of two parts with a sharp break. While one part represents the solubility curve for one form, the second part represents that for the other. **At the meeting point of the two curves, the solubility of the two forms is the same and it indicates the transition temperature.** For example, in the diagram for the system sodium sulphate-water, the solubility curves of Na_2SO_4 (rhombic) and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ meet at 32.2°C . Thus 32.2°C is the transition temperature where $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ changes to Na_2SO_4 .

(4) Cooling curve method

There is often an evolution or absorption of heat when one form passes to the other. Suppose that form A is converted into form B on heating. Now let B be allowed to cool and a curve obtained by plotting the temperature against the time. **The otherwise steady curve has a distinct break at a temperature corresponding to the transition point because here heat is evolved from B .**

This method is suitable for determining the transition temperature between different hydrates of a salt or between a hydrate and an anhydrous salt (e.g., $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to Na_2SO_4), or for different forms of a metal.

THE WATER SYSTEM

Under normal conditions the system 'water' is a **three-phase, one-component system**. The three phases involved are *liquid water*, *ice*, *water vapour*. All these phases can be represented by one chemical entity H_2O and hence one component of the system. The number of phases which can exist in equilibrium any time depends on the conditions of temperature and pressure. The phase diagram or PT -graph of the system/ water/ice/vapour is shown in Fig. 19.3. The **salient features of the phase diagram** are listed below.

- (1) The Curves OA , OB , OC
- (2) The Triple Point O
- (3) The Areas AOC , AOB , BOC

Let us proceed to discuss the significance of each of these features.

(1) The Curves OA , OB , OC

These three curves meet at the point O and divide the diagram into three regions or areas.

Curve OA , the Vapour Pressure curve of Water. It represents the vapour pressure of liquid water at different temperatures. The two phases *water* and *water vapour* coexist in equilibrium along this curve. The curve OA terminates at A , the critical point (218 atm, temp. 374°C) when the liquid and vapour are indistinguishable from each other and there is left one phase only. When the vapour pressure is equal to one-atmosphere, the corresponding temperature, as indicated on the phase diagram is the boiling point (100°C) of water.

Curve OB , the Sublimation curve of Ice. It shows the vapour pressure of solid ice at different temperatures. The two phases *solid ice* and *vapour* coexist in equilibrium along this curve. At the lower limit the curve OB terminates at absolute zero (-273°C) where no vapour exists.

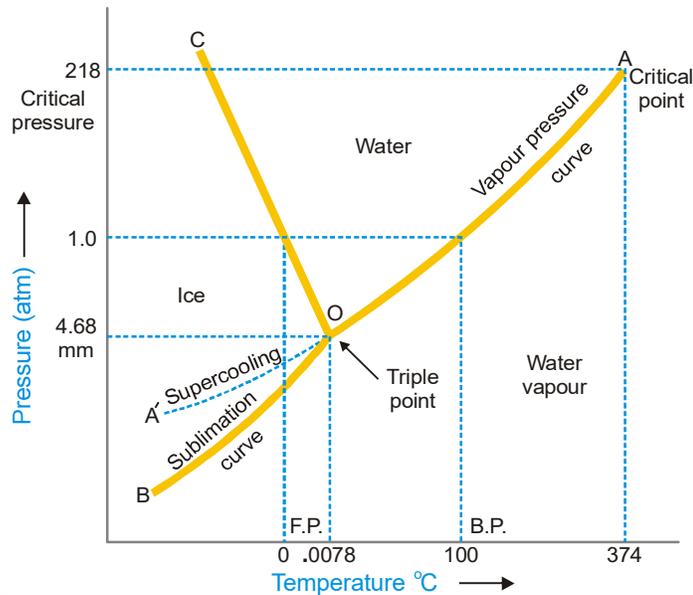


Figure 19.3 The phase diagram of the system 'Water'.

Curve OC, the Fusion curve of Ice. It depicts the effect of pressure on the melting point of ice. Here *ice* and *water* coexist in equilibrium. The fact that *OC* slopes to the left indicates that the melting point of ice decreases with increase of pressure. Since ice melts with decrease in volume by Le Chatelier’s principle the melting point is lowered by an increase of pressure. It may be noted that the 1.0 atmosphere line meets the fusion curve at 0°C which is the normal melting point of ice.

Along the curves *OA*, *OB*, *OC* there are two phases in equilibrium and one component. Therefore,

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

Hence each two-phase system :

- water/water vapour represented by *OA*
- ice/water vapour represented by *OB*
- ice/water represented by *OC*

has one degree of freedom *i.e.*, is **monovariant**.

(2) The Triple point ‘O’

The curves *OA*, *OB* and *OC* meet at the triple point ‘O’ where all the three phases *liquid water/ice/vapour* are in equilibrium. This occurs at 0.0076°C and vapour pressure 4.58 mm Hg. Since there are three phases and one component, we have

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

i.e., the system at the triple point is **nonvariant**. Thus if either pressure or temperature is changed, the three phases would not exist and one of the phases would disappear.

(3) Area AOC, AOB, BOC

The areas or regions between the curves show the conditions of temperature and pressure under which a single phase—**ice, water or vapour** is capable of stable existence. Thus,

Area AOC represents conditions for the one-phase system **water**.

Area AOB represents conditions for the one-phase system **water vapour**.

Area BOC represents conditions for the one-phase system **ice**.

In all the three areas there being one-phase and one-component, we have

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

Thus each system *water*, *water vapour*, or *ice* has 2 degrees of freedom *i.e.*, the system is **bivariant**.

(4) Metastable system : Supercooled Water/Vapour System

The vapour pressure curve of water AO can be continued past the triple point as shown by the dashed line OA' . That is, water can be *supercooled* by carefully eliminating solid particles. The supercooled water/vapour system is metastable (unstable). It at once reverts to the stable system ice/vapour on the slightest disturbance or introducing a crystal of ice.

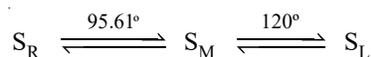
THE SULPHUR SYSTEM

It is a **one-component, four-phase system**. The four phases are :

- (a) Two solid polymorphic forms :
 - (i) Rhombic Sulphur (S_R)
 - (ii) Monoclinic Sulphur (S_M)
- (b) Sulphur Liquid (S_L)
- (c) Sulphur Vapour (S_V)

All the four phase can be represented by the only chemical individual 'sulphur' itself and hence one component of the system.

The two crystalline forms of sulphur S_R and S_M exhibit enantiotropy with a transition point at 95.6°C . Below this temperature S_R is stable, while above it S_M is the stable variety. At 95.6°C each form can be gradually transformed to the other and the two are in equilibrium. At 120°C , S_M melts. Thus,



The phase diagram for the sulphur system is shown in Fig. 19.4. The **salient features of the phase diagram** are described below.

- (i) The six curves AB , BC , CD , BE , CE , EG
- (ii) The three Triple points B , C , E
- (iii) The four areas :

ABG marked 'solid Rhombic'

BEC marked 'solid Monoclinic'

$GECD$ marked 'liquid Sulphur'

$ABCD$ marked 'Sulphur vapour'

Let us now proceed to discuss the significance of these features :

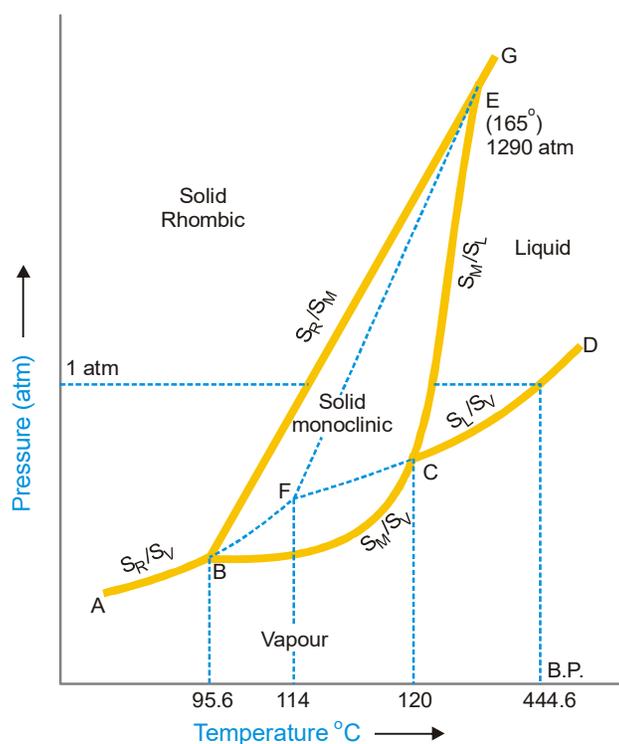
(1) The curves AB , BC , CD , BE , CE , EG

These *six curves* divide the diagram into *four* areas.

Curve AB , the Vapour Pressure curve of S_R . It shows the vapour pressure of solid rhombic sulphur (S_R) at different temperatures. Along this curve the two phases S_R and sulphur vapour (S_V) are in equilibrium. The system S_R/S_V has one degree of freedom,

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

i.e., it is *monovariant*.



■ **Figure 19.4**
The phase diagram of the system 'Sulphur'.

Curve BC, the Vapour Pressure curve of S_M . It shows variation of the vapour pressure of monoclinic sulphur (S_M) with temperature. S_M and S_V coexist in equilibrium along this curve. The system S_M/S_V is *monovariant*.

Curve CD, the Vapour Pressure curve of S_L . It depicts the variation of the vapour pressure of liquid sulphur (S_L) with temperature. S_L and S_V are in equilibrium along CD . The two phase system S_L/S_V is *monovariant*. One atmosphere line meets this curve at a temperature (444.6°C) which is the boiling point of sulphur.

Curve BE, the Transition curve. It shows the effect of pressure on the transition temperature for S_R and S_M . As two solid phases are in equilibrium along the curve, the system S_R/S_M is *monovariant*. The transformation of S_R and S_M is accompanied by increase of volume (density of $S_R = 2.04$; $S_M = 1.9$) and absorption of heat *i.e.*,



Thus the increase of pressure will shift the equilibrium to the left (*Le Chatelier's Principle*) and the transition temperature will, therefore, be raised. This is why the line BE slopes away from the pressure axis showing thereby that the transition temperature is raised with increase of pressure.

Curve CE, the Fusion curve of S_M . It represents the effect of pressure on the melting point of S_M . The two phases in equilibrium along this curve are S_M and S_L . The system S_M/S_L is *monovariant*. As the melting or fusion of S_M is accompanied by a slight increase of volume, the melting point will rise by increase of pressure (*Le Chatelier's principle*). Thus the curve CE slopes slightly away from the pressure axis. The curve ends at E because S_M ceases to exist beyond this point.

Curve EG, the Fusion curve for S_R . Here the two phases in equilibrium are S_R and S_L . The number of phases being two, the system S_R/S_L is *monovariant*.

(2) The Triple points B, C, E

Triple point B. This is the meeting point of the three curves AB , BC and BE . Three phases, solid S_R , solid S_M and S_V are in equilibrium at the point B. There being three phases and one component, the system $S_R/S_M/S_L$ is *nonvariant*.

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

At B, S_R is changed to S_M and the process is reversible. Thus the temperature corresponding to B is the *transition temperature* (95.6°C).

Triple point C. The curves BC , CD , CE meet at this point. The three phases in equilibrium are S_M , S_L and S_V . There being three phases and one component, the system $S_M/S_L/S_V$ is *nonvariant*. The temperature corresponding to C as indicated on the phase diagram is 120°C. This is the melting point of S_M .

Triple point E. The two lines CE and BE , having different inclinations away from the pressure axis, meet at E where a third line EG also joins. The three phases S_R , S_M and S_L are in equilibrium and the system at the point E is *nonvariant*. This point gives the conditions of existence of the system $S_R/S_M/S_L$ at 155°C and 1290 atmospheres pressure.

(3) The Areas

The phase diagram of the sulphur system has **four areas** or **regions**. These are labelled as rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour. These represent single phase systems which have two degrees of freedom,

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

That is, each of the systems S_R , S_M , S_L , and S_V are *bivariant*.

(4) Metastable Equilibria

The change of S_R to S_M takes place very slowly. If enough time for the change is not allowed and S_R is heated rapidly, it is possible to pass well above the transition point without getting S_M . In that case, there being three phases (S_R , S_L , S_V) only and one component, the phase diagram, like that of water system, will consist of three curves, one triple point and three areas.

The dashed curve BF, the Vapour Pressure curve of metastable S_R . This is a continuation of the vapour pressure curve AB of stable S_R . The metastable phases S_R and S_V are in equilibrium along this curve. It is a *monovariant system*.

The dashed curve CF, the Vapour Pressure curve of supercooled S_L . On supercooling liquid sulphur, the dashed curve CF is obtained. It is, in fact, the back prolongation of DC . The curve CF represents the metastable equilibrium between supercooled S_L and S_V . Thus it may be designated as the vapour pressure curve of supercooled S_L . It meets the dashed curve BF at F.

The dashed curve FE, the Fusion curve of metastable S_R . The two metastable phases S_R and S_L are in equilibrium along this curve and the system is *monovariant*. This shows that the melting point of metastable S_R is increased with pressure. Beyond E, this curve depicts the conditions for the stable equilibrium S_R/S_L as the metastable S_R disappears.

The metastable Triple point F. At this point, three metastable phases S_R , S_L and S_V are in equilibrium. The system is a metastable triple point with no degree of freedom. The corresponding temperature is the melting point of metastable S_R (114°C).

TWO-COMPONENT SYSTEMS

When a single phase is present in a two-component system, the degree of freedom is three,

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

This means that three variables must be specified in order to describe the condition of the phase. Thus in such a system, in addition to pressure and temperature the concentration of one of the

components has also to be given. For graphic representation of these variables, three coordinate axes at right angles to each other would be required. Therefore the phase diagram obtained would be a solid model.

For the sake of having simple plane diagrams we generally consider only two variables, the third one being a constant. For example, for a solid/liquid equilibrium, the gas phase is usually absent and the effect of pressure on the equilibrium is very small. Thus when a two-component system consists of solid and liquid phases only, the effect of pressure may be disregarded. Then it is necessary to take into account the remaining variables *viz.*, temperature and concentration. **Such a solid/liquid system with the gas phase absent is called a condensed system.**

The experimental measurements of temperature and concentration in condensed systems are usually carried out under atmospheric pressure. Since the degree of freedom in such a case is reduced by one, we may write the **Reduced Phase rule** as

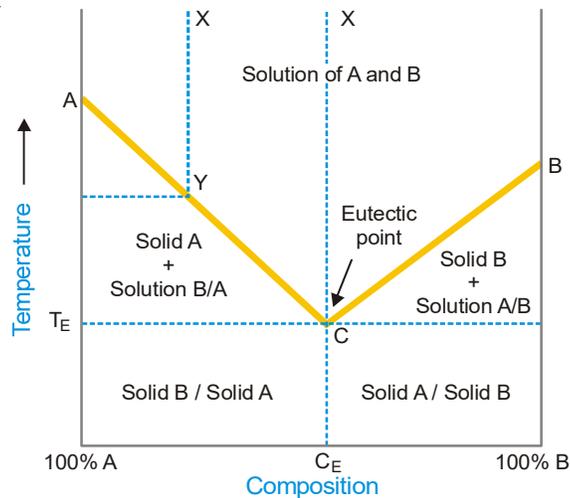
$$F' = C - P + 1$$

where F' gives the remaining degrees of freedom of the system. The reduced phase rule is more convenient to apply to solid/liquid two-component condensed system.

Since the only variables for two-component solid/liquid systems are temperature and composition, the phase diagrams for such systems consist of Temperature-Concentration graphs (*TC graphs*).

Simple Eutectic Systems

The general form of the phase diagram of such a 2-component condensed system is shown in Fig. 19.5. Here the two components *A* and *B* are completely miscible in the liquid state, and these solutions on cooling yield only pure *A* or pure *B* as solid phases.



■ **Figure 19.5**
Simple Eutectic diagram.

The diagram consists of :

Curve AC; the Freezing point curve of A. The point *A* represents the freezing point of *A*. The curve *AC* shows that the freezing point of *A* falls by the addition of *B* to *A*. Thus along this curve, the solid *A* is in equilibrium with the liquid solution of *B* in *A*.

Curve BC; the Freezing point curve of B. The point *B* shows the freezing point of *B*. The curve *BC* exhibits the fall of freezing point by the addition of *A* to *B*. Along this curve, the solid *B* is in equilibrium with the liquid solution of *A* in *B*.

Applying the reduced phase rule equation to the equilibria represented by the curve AC and CB *i.e.*, solid A /solution and solid B /solution respectively, we have

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

The degree of freedom is one *i.e.*, both equilibria are *monovariant*.

The Eutectic point C . The two curves AC and BC meet at the point C . Here both the solids A and B must be in equilibrium with the solution phase (solution of A and B). The number of phases is 3. By applying the reduced phase rule equation, we have

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

Thus the system represented by the point C is *nonvariant*. In other words, both the temperature and composition of the system solid A /solid B /solution are fixed.

The mixture of components A and B as at point C melts at the lowest temperature T_E indicated on the graph. The point C is therefore, called **the Eutectic point** (Greek *eutectos* = easy melting). The corresponding composition (C_E) and temperature (T_E) are known as the **eutectic composition** and the **eutectic temperature** respectively of the system.

The **eutectic mixture, although it has a definite melting point, is not to be regarded as a compound**. The reasons are : (i) the components are not in stoichiometric proportions; and (ii) on examination under a microscope these reveal the existence of separate crystals of the components.

The Area above the curves AC and BC . Here the two components A and B are present as *liquid solutions* of varying compositions. As a homogeneous solution of A and B constitutes one phase only, this system is *bivariant*.

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

Therefore to define the system at any point in this area, both temperature and composition have to be specified.

Effect of Cooling

When the A/B solution at any point in the area above ACB is cooled, the cooling dashed line meets the curve AC , say at Y . Here solid A separates and the equilibrium shifts down along the curve AC . The change of composition and temperature continues till the eutectic point C is reached when solid B also separates. Thus in the area below AC and above T_E line, there exist two phases *viz.*, solid A and solution A/B , and the system is *bivariant*. Similarly, cooling of solution B/A on the other side of eutectic, on reaching the curve BC would yield solid B /solution system. Thus the area below BC up to T_E line would represent solid B and solution.

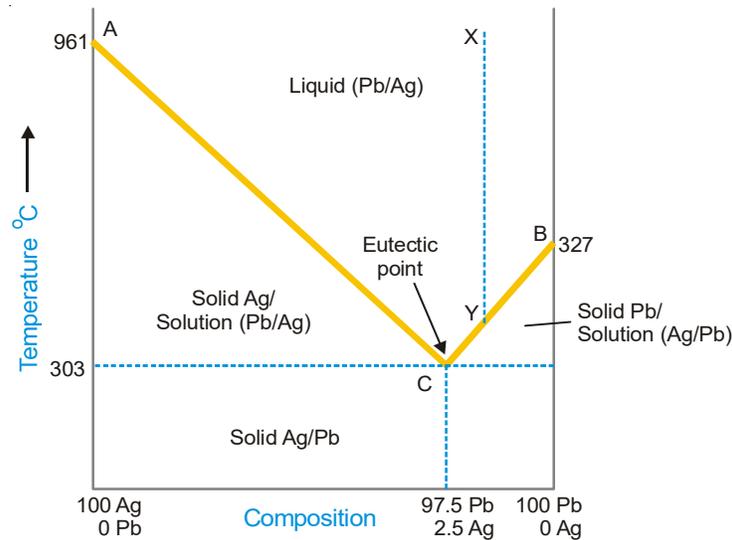
If the solution just above the eutectic point is cooled, a solid mixture (*eutectic mixture*) of eutectic composition CE , will be obtained straightaway.

Since below T_E line no liquid can exist, the entire area below this line would represent the system solid A /solid B .

THE SILVER-LEAD SYSTEM

This system has **two components** and **four phases**. The phases are : (i) solid silver; (ii) solid lead; (iii) solution of molten silver and lead; and (iv) vapour.

The boiling points of silver and lead being considerably high, the vapour phase is practically absent. Thus Ag/Pb is a condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need consider only the two remaining variables, namely the temperature (T) and concentration (C). The complete TC diagram of the system Ag/Pb is shown in Fig. 19.6.



■ **Figure 19.6**
The phase diagram of Ag/Pb system.

The salient features of the diagram are :

- Two curves, AC and BC
- Eutectic point, C
- Three areas : (i) above ACB ; (ii) below AC ; (iii) below BC

Curve AC; the Freezing point curve of Ag. A represents the freezing point or melting point of solid silver (961°C) and the curve AC shows that the addition of lead lowers the melting point along it. The phases in equilibrium along AC are solid silver and solution of silver and lead. Applying the reduced phase rule equation

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

Thus the system Ag/solution is *monovariant*.

Curve B; the Freezing point curve of Pb. B represents the melting point of solid lead (327°C) and the curve BC shows that the melting point is lowered by addition of silver. The phases in equilibrium along BC are solid lead and solution. The system is *monovariant*.

The Eutectic point C. The curves AC and BC intersect at C , which is called the *eutectic point*. Here three phases solid Ag, solid Pb, and solution are in equilibrium. Applying the reduced phase rule equation

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

Thus the system Ag/Pb/solution at C is *nonvariant*. Both the variables, temperature (303°C) and composition (97.5% Pb, 2.5% Ag) are fixed. If you raise the temperature above the eutectic temperature, the solid phases Ag and Pb disappear and if you cool below it, you will land in the solid Ag/Pb area where solution phase is nonexistent.

The Area above AOC. This region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule equation, we have

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

Thus the system solution Ag/Pb is *bivariant*.

The area below AC represents the phases Ag + solution, while that below BC the phases Pb + solution. The area below the temperature 303° , represents solid Ag + solid Pb. All these areas

have two phases and one degree of freedom,

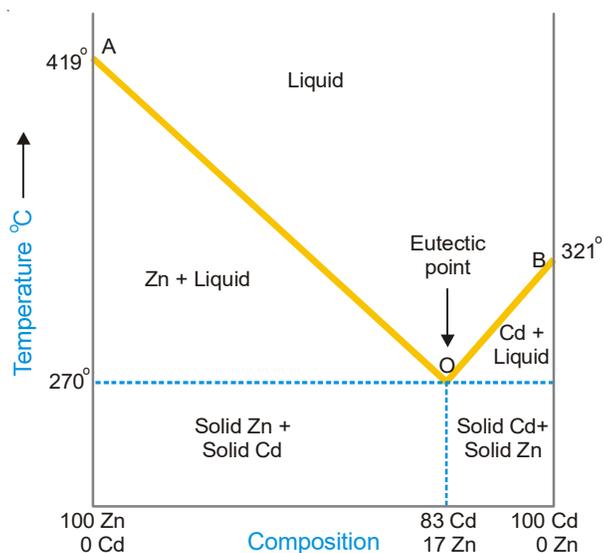
$$F = C - P + 1 = 2 - 2 + 1 = 1$$

Pattinson's Process for the Desilverisation of Argentiferous Lead

This process of recovery of silver from argentiferous lead is based on the facts contained in the diagram (Fig. 19.6). The argentiferous lead containing small amount of silver (less than 0.1%) is melted well above the melting temperature of pure lead (327°C). Let the point *X* represent the system 'molten lead' on the diagram. It is then allowed to cool when the temperature of the melt falls along the dashed line *XY*. As the temperature corresponding to *Y* on the curve *BC* is reached solid lead begins to separate and the solution would contain relatively larger amount of silver. On further cooling, more of lead separates and we travel along the curve *BC* until the eutectic point *C* is reached. Lead is continuously removed by means of ladles and the percentage of silver in the melt goes on increasing. At *C*, an alloy containing 2.5% Ag and 97.5% Pb is obtained. This is treated for the recovery of silver profitably.

THE ZINC-CADMIUM SYSTEM

This is another example of a metal/metal system with a eutectic. The phase diagram is shown in Fig 19.7 which is similar to the one for silver/lead system. It consists of :



■ **Figure 19.7**
Phase diagram of Zn-Cd system.

Curve AO; the Freezing point curve of Zinc. *A* represents the freezing point (or melting point) of zinc (419°C). The curve *AO* shows that the melting point of zinc is lowered by the addition of cadmium. The phases in equilibrium along *AO* are solid zinc and liquid solution of zinc and cadmium. Applying the reduced phase rule equation,

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

Thus the system solid zinc/solution is *monovariant*.

Curve BO; the Freezing point curve of Cadmium. The point *B* represents the melting point of cadmium (321°C). The curve *BO* shows the fall of melting point of cadmium on the addition of zinc. Along this curve, solid cadmium is in equilibrium with the liquid solution of zinc and cadmium.

Applying the reduced phase rule equation to the equilibrium cadmium/solution,

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

Thus the degree of freedom is one and the equilibrium is *monovariant*.

The Eutectic point *O*. The curves *AO* and *BO* meet at *O*. Here, solid zinc, solid cadmium and solution are in equilibrium. The number of phases is, therefore, three.

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

Thus the system at point *O* is *nonvariant*. The point *O* is called the **eutectic point**. Both the temperature and composition being fixed, the system has no degree of freedom. The eutectic temperature is 270° and the eutectic composition is 83% cadmium 17% zinc.

The Area above *AO*. In this area, both the components zinc and cadmium are present as liquid solution of varying composition. The solution of the two metals being homogeneous, constitutes one phase only. Thus the system represented by the area above *AO* is *bivariant*.

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

The Area above *BO*. In this area, zinc and cadmium exist as liquid solution. The composition of the solution is indicated on the composition axis. The liquid solution, regardless of its composition, represents one phase only. Thus the system in the area above *BO* is *bivariant*.

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

The effect of cooling. If the solution in the area above *AO* is cooled, zinc separates as the curve itself is reached. This continues till the point *O* when the solid eutectic mixture (83% Cd + 17% Zn) separates. Similarly, the solution above *BO* on cooling allows the separation of cadmium. This continues till the point *O* is reached at 270°C and eutectic mixture separates. As clear from the diagram, the area below the curve *AO* represents zinc and solution; the area below *BO* shows cadmium and solution. The area below the eutectic temperature represents the system solid zinc/solid cadmium.

POTASSIUM IODIDE–WATER SYSTEM

It has **four phases** : (i) Solid KI ; (ii) Solution of KI in water ; (iii) Ice; and (iv) Vapour. Only two chemical constituents KI and H₂O being necessary to depict the composition of all the four phases, it is a **two-component system**.

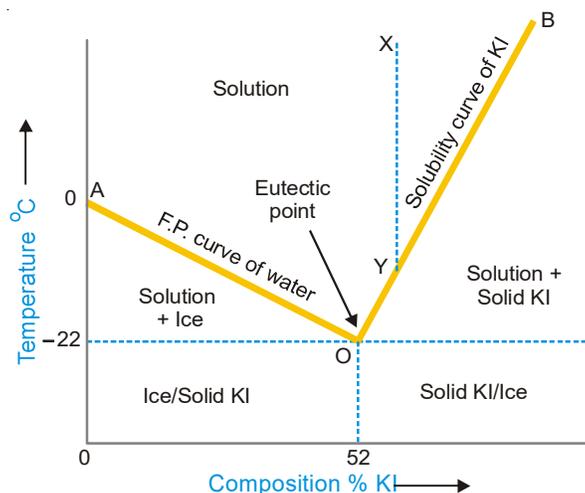
Since the conditions for the existence of the various phases are studied at atmospheric pressure the vapour phase is ignored and the system KI-H₂O is regarded as a *condensed system*. Pressure being constant, the two variables, temperature and concentration will be considered. The *TC* diagram of the system is shown in Fig. 19.8. It consists of :

- (a) The Curves *AO* and *OB*
- (b) The Eutectic Point *O*
- (c) The area above *AOB* and the areas below the curves *OA* and *BO*

The Curve *AO*; the Freezing point curve of Water. The point *A* represents the freezing point of water or the melting point of ice (0°C) under normal conditions. The curve *AO* shows that the melting point of ice falls by the addition of solid KI. As more and more of KI is added, the concentration of solution and the melting temperature changes along the curve *AO*. The phases in equilibrium along the curve *AO* are ice and solution. Applying the reduced phase rule equation to the condensed system ice/solution, we have

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

Thus the system is *monovariant*.



■ **Figure 19.8**
The phase diagram of the system KI-H₂O.

The Eutectic point. The lowest point attainable by the addition of KI along the curve *OA* is *O*. Here the solution becomes saturated with KI and the solid KI appears as the third phase. This point is termed the *Eutectic Point* or *Cryohydric Point* as one of the components in the system is water. Applying the reduced phase rule equation to the system ice/solid KI/solution at point *O*.

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

Hence the system is *nonvariant*. That is, both the temperature (-22°C) and composition (52% KI + 48% ice) are fixed.

The Curve *BO*; the Solubility curve of KI. At *O*, the solution is saturated with KI. Thus the curve *BO* depicts the effect of temperature on the concentration of saturated solution or the solubility of KI. The phases in equilibrium along the curve are solid KI and solution. Applying the reduced phase rule equation, we have

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

That is, the condensed system solid KI/solution is *monovariant*.

The Area above *AOB*. It represents the single phase system 'solution'. Applying the phase rule equation,

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

Therefore the system is *bivariant*.

As labelled in the diagram, the area below *AO* shows the existence of ice and solution, while the area below *BO* depicts the presence of solid KI and solution. Below the eutectic temperature line, there can exist ice and solid KI only.

Cooling Produced by Freezing Mixtures

KI-H₂O is a typical eutectic system with a salt and water as components. Many other salts as sodium chloride, sodium nitrate, ammonium chloride and ammonium nitrate constitute eutectic systems with water and form similar phase diagrams as shown in Fig. 19.8. The facts contained in this diagram explain the **theory of freezing mixtures** which are obtained by mixing salt and ice.

When we add a salt, common salt (NaCl) to melting ice, we follow along the curve *AO*. Thus the addition of salt to the system ice/water produces a continued lowering of temperature until the eutectic point *O* is reached. Thus the lowest temperature attained in this way will be the eutectic

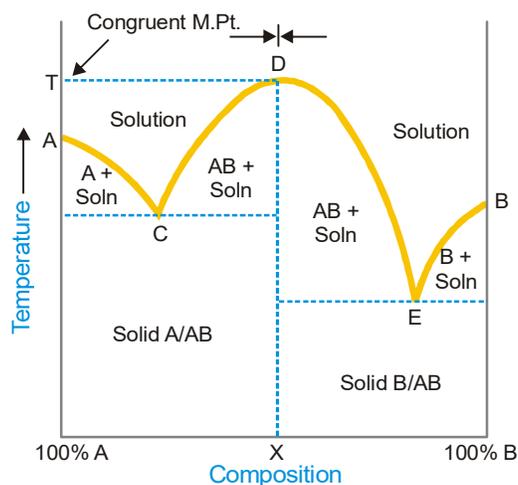
temperature (-22.0°C). Alternatively, we may start with a concentrated solution of the salt represented by point X on the phase diagram. As we withdraw heat by adding ice, we travel along the dashed line XY . At Y which lies on the solubility curve BO , the solution becomes saturated with the salt. On further withdrawing heat, we go along with the curve BO until the eutectic point is reached. Thus the same minimum temperature can be attained with a freezing mixture, whether we add salt to ice or ice to salt solution. The eutectic temperatures of some salt/ice systems are listed below.

System	Eutectic Temperature
$\text{NH}_4\text{Cl} + \text{ICE}$	-16.0°C
$\text{NaCl} \cdot 2\text{H}_2\text{O} + \text{ICE}$	-22.0°C
$\text{KNO}_2 + \text{ICE}$	-2.6°C
$\text{NaNO}_2 + \text{ICE}$	-18.1°C
$\text{KCl} + \text{ICE}$	-11.4°C

Systems in which two components form a solid compound

So far we have studied systems in which the two components exist as separate entities whether in the solid or solution phase. There are a number of systems known, in which two metals form an *intermetallic compound*, or a salt and water form a *solid hydrate*.

Let us consider a general case with two components A and B which form a stable compound AB . The phase diagram for such a system will be of the type shown in Fig. 19.9.



■ **Figure 19.9**
Compound formation with congruent melting point.

The system will involve three solid phases, A , B and AB . The fourth phase will be a liquid (or solution) containing varying concentration of A and B . There are three freezing point or melting point curves *viz.*, AC , CDE and EB . The various phases in equilibrium along these curves and in different regions are labelled in the phase diagram.

What is Congruent Melting Point?

Along the freezing point curve CDE of the compound AB , solid AB is in equilibrium with the solution phase. At the maximum point D of this curve, the composition of the solid compound and the liquid phase in contact is the same, which is indicated by X on the composition axis. The corresponding temperature T , therefore, coincides with the melting point of the compound AB .

When the solid compound AB and the liquid phase have identical composition at the maximum point on the freezing point curve, the corresponding temperature is said to be the **Congruent Melting Point of the compound**.

At point D since both the phases have the same composition, the system has one component only. Hence it is *nonvariant*.

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

The diagram in Fig. 19.9 has the appearance of two simple eutectic diagrams joined together at the position of arrows. The diagram to the left represents the eutectic system A/AB , while that on the right the system AB/B . The phase diagram of the system Zinc-Magnesium is exactly of the type shown in Fig. 19.9.

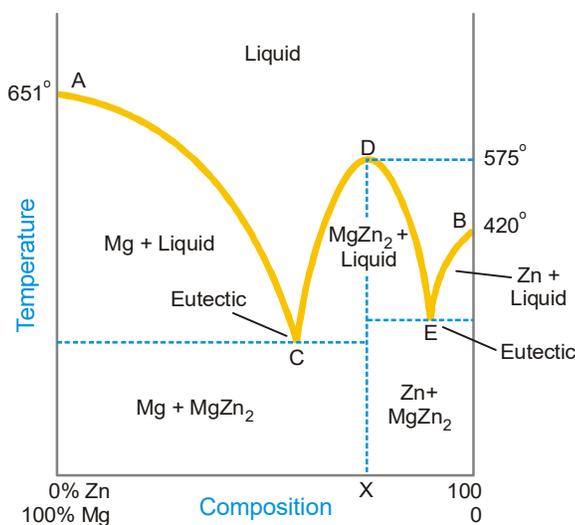
The salt-water systems often involve the formation of several compounds (hydrates). For example, the system Ferric chloride-Water forms as many as four hydrates. Thus the composite phase diagram could be regarded as made of four simple eutectic diagrams.

Some common 2-component systems involving the formation of one or more compounds with congruent melting points are discussed below.

THE MAGNESIUM-ZINC SYSTEM

It is a typical 2-component system which involves the formation of an intermetallic compound $MgZn_2$. It has four phases : solid magnesium (Mg), solid zinc (Zn), solid $MgZn_2$ and the liquid solution of Mg and Zn.

The complete phase diagram of the system magnesium-zinc is shown in Fig. 19.10. It appears to be made of two simple eutectic diagrams. The one toward the left represents the eutectic system $Mg-MgZn_2$, while the one to the right the system $Zn-MgZn_2$.



■ **Figure 19.10**
The phase diagram of the system $KI-H_2O$.

The curves AC , CDE and BE . AC is the freezing point curve of magnesium; BE is the freezing point curve of zinc; and CDE is that of the compound $MgZn_2$.

The curve AC shows that the melting point of magnesium ($651^\circ C$) is lowered on the addition of zinc. This continues until the point C is reached. Here a new phase, solid $MgZn_2$ appears.

The curve CD shows the increase of concentration of zinc in the melt with the rise of temperature. At the maximum point D , the composition of the melt and the solid compound becomes the same *i.e.*,

MgZn₂. The point D, therefore, represents the melting point of MgZn₂ (575°C). The curve DE now shows the lowering of the melting point with the addition of zinc until the lowest point is attained. Here solid zinc appears.

The curve BE exhibits that the melting point of zinc (420°C) falls with the addition of magnesium until the point E is reached.

Along the freezing point curves AC, CDE and BE, there are two phases in equilibrium viz., one solid phase (Mg, Zn, or MgZn₂) and the other liquid phase. Applying the reduced phase rule equation, we have

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

This shows that the system Mg/liquid, Zn/liquid and MgZn₂/liquid are all *monovariant*.

Eutectic points C and E. There are two eutectic points in the phase diagram. The systems at the points C and E have two components and three phases in equilibrium.

Phases Present

C	Solid Mg, solid MgZn ₂ , Liquid
E	Solid Zn, solid MgZn ₂ , Liquid

These systems are, therefore, *nonvariant*.

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

Congruent Melting Point. As already stated, the composition of the compound MgZn₂ and the melt at D is identical. The corresponding temperature is the *congruent melting point* of the compound. Here the system has two phases viz., the solid compound and the melt. Both these can be represented by one component (MgZn₂). Therefore the system at D is *nonvariant*,

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

The Areas. The area above the curves AC, CDE and BE represents the solution of magnesium and zinc (the melt). The single phase system at any point in this area is *bivariant*.

The phases present in the other regions of the phase diagram are as labelled.

THE FERRIC CHLORIDE–WATER SYSTEM

This provides an example of a 2-component system in which many compounds (hydrates) are formed. It is a composite system made of several simple eutectic systems.

Seven-phase condensed system. Ferric chloride (Fe₂Cl₆) forms four stable crystalline hydrates :

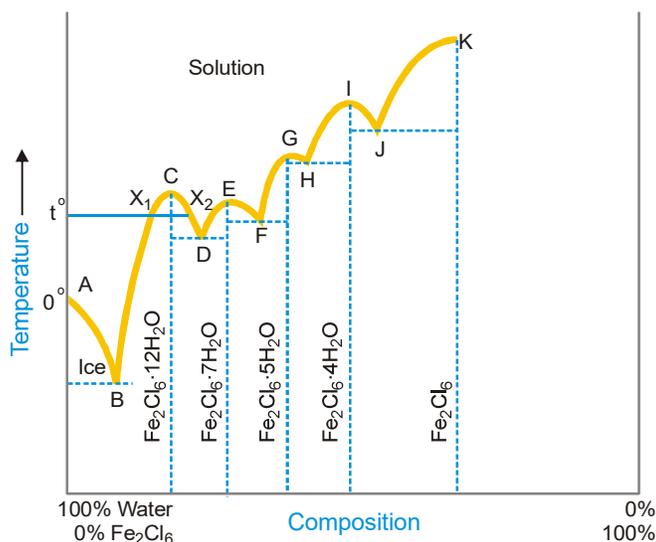
Formula	Abbreviated Name	Abbreviated Formula
Fe ₂ Cl ₆ .12H ₂ O	Dodecahydrate	12H ₂ O
Fe ₂ Cl ₆ .7H ₂ O	Heptahydrate	7H ₂ O
Fe ₂ Cl ₆ .5H ₂ O	Pentahydrate	5H ₂ O
Fe ₂ Cl ₆ .4H ₂ O	Tetrahydrate	4H ₂ O

The other three phases involved are ice, anhydrous ferric chloride and solution. Since all measurements of temperature and concentration are made at atmospheric pressure, the vapour phase is ignored and the system Fe₂Cl₆/H₂O is considered a **condensed system**.

Two components. As the composition of all the seven phases can be represented by the constituents Fe₂Cl₆ and H₂O, it is a two-component system.

Phase Diagram of Fe₂Cl₆/H₂O System

The phase diagram of the ferric chloride-water system is shown in Fig. 19.11.



■ **Figure 19.11**
The Ferric chloride-Water system.

The Curves. The point *A* represents the normal freezing point of water. The curve *AB* shows the lowering of freezing point on the addition of ferric chloride and hence is named as the **freezing point curve of water**. The freezing point falls till the point *B* is reached where a new phase $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ separates. Now as the temperature is raised and more of Fe_2Cl_6 is added, we travel along the curve *BCD*. $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ and saturated solution are in equilibrium along this curve which is, therefore, called the **solubility curve of dodecahydrate**. It will be noted that both the increase as also the decrease in the proportion of Fe_2Cl_6 in the solution at *C* will cause a lowering of solubility. Thus at a temperature such as t° , the $12\text{H}_2\text{O}$ has two distinct solubilities in water, X_1 and X_2 . **This phenomenon of having two solubilities at the same temperature, characteristic of systems producing solid compounds, is called retroflex solubility.**

The solubility curve *BCD* of $12\text{H}_2\text{O}$ terminates at *D* where another hydrate $7\text{H}_2\text{O}$ separates. The curve *DEF* is the solubility curve of the heptahydrate. At *F*, the $5\text{H}_2\text{O}$ appears and *FGH* is its solubility curve. At *H*, $4\text{H}_2\text{O}$ separates and *HIJ* is its solubility curve. At *J*, solid ferric chloride (Fe_2Cl_6) appears and *JK* is the solubility curve of the anhydrous salt.

Along the curves *AB*, *BCD*, *DEF*, *FGH*, *HIJ* and *JK*, one solid phase and one liquid (solution) phase are in equilibrium. Therefore applying the reduced phase rule equation we have

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

Hence the systems ice/solution, $12\text{H}_2\text{O}$ /solution, $7\text{H}_2\text{O}$ /solution, $5\text{H}_2\text{O}$ /solution, $4\text{H}_2\text{O}$ /solution, and Fe_2Cl_6 /solution represented by the various curves are *monovariant*.

The Congruent Melting Points. At points *C*, *E*, *G*, *I* the composition of the solution in equilibrium with the respective hydrate is identical. These points, therefore, represent the congruent melting points of the different hydrates (Table 19.1).

Since a solid phase (hydrate) and liquid phase (solution) are identical at the congruent melting point, the system at points *C*, *E*, *G*, *I* has two phases and one component. It is, therefore, *nonvariant*,

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

TABLE 19.1. CONGRUENT MELTING POINTS OF HYDRATES OF Fe_2Cl_6

Point	Congruent m.p.	Hydrate
<i>C</i>	37°	12H ₂ O
<i>E</i>	32.5°	7H ₂ O
<i>G</i>	56°	5H ₂ O
<i>I</i>	73.5°	4H ₂ O

The Eutectic points. The phase diagram of the system $\text{Fe}_2\text{Cl}_6\text{-H}_2\text{O}$ could be split into five simple eutectic diagrams as shown by dashed lines in Fig. 19.11. The point *A* represents the melting point of ice, while *C* represents the congruent melting point of 12H₂O. The eutectic diagram is made of the curve *AB*, the melting point curve of ice and the curve *CB*, the melting point curve of 12H₂O. The lowest point attainable on these curves, *B*, is the eutectic point. Similarly the other eutectic points in the phase diagram are *D, F, H, J*.

Eutectic Point	Temperature	Phases in Equilibrium
<i>B</i>	-55°	ice, 12H ₂ O, solution
<i>D</i>	27.4°	12H ₂ O, 7H ₂ O, solution
<i>F</i>	30°	7H ₂ O, 5H ₂ O, solution
<i>H</i>	55°	5H ₂ O, 4H ₂ O, solution
<i>J</i>	66°	4H ₂ O, Fe_2Cl_6 , solution

At each of these eutectic points, the system has three phases and two components. Applying the reduced phase rule equation, we have

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

That is, the system is *nonvariant*.

THE SODIUM SULPHATE-WATER SYSTEM

Sodium sulphate forms two hydrates $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (decahydrate) and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (heptahydrate). Furthermore, the anhydrous salt can exist in two enantiotropic crystalline forms, *viz.*, **rhombic** and **monoclinic**. The remaining phases are solid ice, solution, and vapour. Since all determinations are made at atmospheric pressure, the vapour phase is ignored. Thus the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ is a **six phase condensed system**.

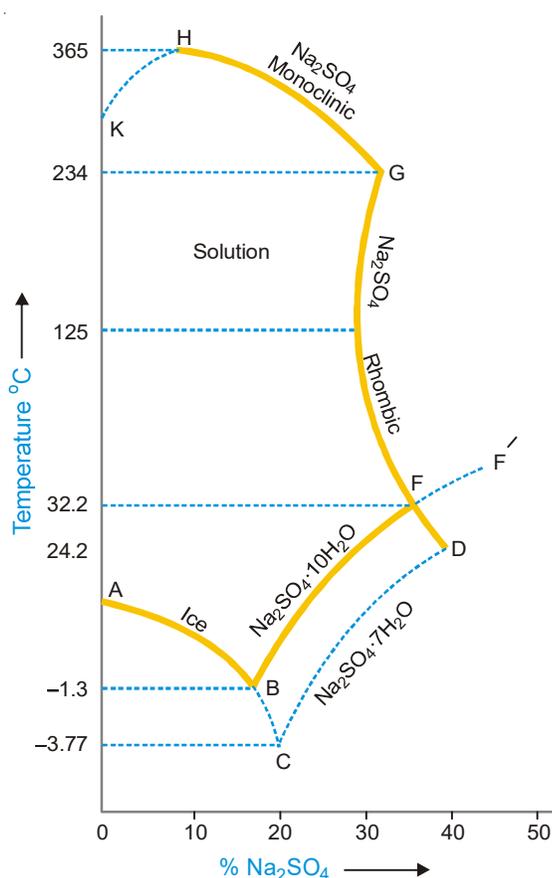
The composition of all the six phases can be represented by the constituents Na_2SO_4 and H_2O . Hence the sodium sulphate-water system has **two components**.

The phase diagram (*or TC graph*) is shown in Fig. 19.12.

The Curve *AB*, the Melting point curve of ice. The point *A* (0°C) is the melting point of ice. The curve *AB* shows the lowering of melting point of ice on the addition of anhydrous Na_2SO_4 . The two phases in equilibrium along *AB* are ice and solution. Applying the reduced phase rule equation,

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

That is the system ice/solution is *monovariant*.



■ **Figure 19.12**
Sodium Sulphate-Water system.

The Eutectic point B. At *B*, a new solid phase $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ appears. This is the lowest temperature (-1.3°C) attainable or the **Eutectic Point** where three phases, namely, ice, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and solution can coexist in equilibrium. Applying reduced phase rule equation,

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

and the system is *nonvariant*.

The Curve BF, the Solubility curve of $10\text{H}_2\text{O}$. If the system at *B* is heated and more of anhydrous Na_2SO_4 added, we travel along the curve *BF*. Along this curve, saturated solution of sodium sulphate and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is in equilibrium. Thus the curve *BF* shows that the solubility of $10\text{H}_2\text{O}$ increases with temperature until the point *F* is reached. The system $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ /solution is *monovariant*.

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

The Transition point F. At *F*, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ loses water and changes to the anhydrous rhombic Na_2SO_4 . Thus, this point represents the **transition temperature** (32.2°C).



This temperature may also be regarded as the **incongruent melting point** of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as the composition of the liquid phase (solution) is different from that of the solid hydrate in equilibrium.

At *F*, there are two components and three phases *viz.*, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4 and the solution. Hence the system is *nonvariant*.

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

The Curve FG , the Solubility curve of rhombic Na_2SO_4 . When the system at F is heated, ultimately all the $10\text{H}_2\text{O}$ will disappear and we pass along the curve FG , the solubility curve of anhydrous rhombic Na_2SO_4 . The curve shows that the solubility decreases up to 125°C with rise of temperature and then increases till we reach the point G . At G (234°C), the rhombic Na_2SO_4 changes into the monoclinic form. Thus G represents a transition point where *enantiotropic transformation* occurs. With two components and three phases in equilibrium, the system at G is *nonvariant*.

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

The Curve GH , the Solubility curve of monoclinic Na_2SO_4 . On continued heating the system at G , ultimately the rhombic Na_2SO_4 completely changes into the monoclinic Na_2SO_4 . Then we pass along the curve GH , which is the solubility curve of the monoclinic salt. This shows that the solubility falls gradually with rise in temperature up to 365°C , the critical point of the solution. The system along GH has two components and two phases, namely, Na_2SO_4 monoclinic and solution. Thus,

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

the system is *monovariant*.

Metastable Equilibria of $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ System

The metastable equilibria of the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ are shown by dashed lines in the phase diagram.

- The Curve FF' .** If enough time is not allowed at F , $10\text{H}_2\text{O}$ is not changed into anhydrous rhombic Na_2SO_4 . The curve FF' , therefore, is the *solubility curve of metastable $10\text{H}_2\text{O}$* .
- The Curve BC .** If by careful cooling, $10\text{H}_2\text{O}$ does not separate at B , we pass along the dashed curve BC . This is the *freezing point curve of metastable supercooled solution saturated with respect to $10\text{H}_2\text{O}$* .
- The Eutectic C .** At C (-3.77°), metastable $7\text{H}_2\text{O}$ appears. Therefore, the point C is the eutectic point where three metastable phases *viz.*, supercooled solution, ice, and $7\text{H}_2\text{O}$ coexist in equilibrium.
- The Curve CD .** By raising the temperature of the system at C , we pass along the dashed curve CD , the solubility curve of metastable $7\text{H}_2\text{O}$.
- The Curve FD .** When a saturated solution with respect to rhombic Na_2SO_4 is cooled quickly $10\text{H}_2\text{O}$ does not appear at F (32.2°) and we pass on to D . The dashed curve FD is, therefore, *the solubility curve of metastable $10\text{H}_2\text{O}$* .
- The Transition point D .** The point D represents the transition point where the metastable $7\text{H}_2\text{O}$ is changed into metastable rhombic Na_2SO_4 .

EXAMINATION QUESTIONS

- Define or explain the following terms :

(a) Phase rule	(b) Degree of freedom
(c) Phase	(d) Component
- Explain the term component. How many components are present in the following systems?

(a) $\text{Water} \rightleftharpoons \text{Water - vapour}$	(b) $\text{KCl} + \text{Water} \rightleftharpoons \text{KCl hydrate}$
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Answer. (a) 1; (b) 2
- How many phases are present in each of the following systems :