

Topic 3 - Phase Rule

Syllabus: Phase Rule: Gibbs phase rule, Explanation of the terms Phase, Component, Degree of freedom, Phase reactions, types of equilibrium, equilibrium conditions. One component system-Water system, Sulphur system, Two component system- Lead Silver system, Application of Eutectic system, Merit and Demerits of Phase rule.

3.1. Introduction:

The phase rule is an important aspect related to the equilibrium behaviour of heterogeneous systems. By applying phase rule, it is possible to predict quantitatively the effect of change in temperature, pressure or composition on equilibrium.

The phase rule was put forward by American physicist Willard Gibb's in 1874. It states that, For heterogeneous system in equilibrium, **the sum of number of degrees of freedom and number of phases equals number of components plus two.**

Thus, Mathematically, $F+P = C+2$ or $F = C - P + 2$

$$F = C - P + 2$$

Where F – Degrees of freedom, P – Number of phases and C – Number of components.

Explanation of terms –

3.1.1. 'Phase'

A phase may be defined as: Any part of system which is homogenous about itself, physically distinct and mechanically separable from system OR **any homogeneous part of a heterogeneous 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**. (1 phase)

A system consisting of two or more phases is called a **heterogeneous system**. (2 or more phases)

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.

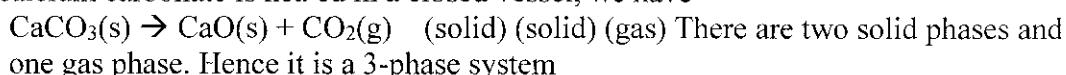
(5) **Aqueous solutions.** An aqueous solution of a solid substance such as sodium chloride (or sugar) is uniform throughout. Therefore, it is a 1-phase system. However, a saturated solution of sodium chloride in contact with excess solid sodium chloride is a 2-phase system.

(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



3.1.2. 'Components'

A term '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 .

Phase Components: Gaseous Mixture = $x \text{ O}_2 + y \text{ N}_2$ 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.

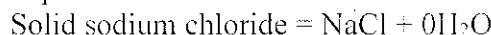
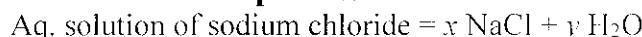
(3) **Sodium chloride solution.** A solution of sodium chloride in water is a 1-phase system. Its composition ($x\text{NaCl}, y\text{H}_2\text{O}$) can be expressed in terms of two chemical individuals, sodium chloride and water.

Phase Components Aq. solution of = $\text{NaCl} + y \text{ H}_2\text{O}$ sodium chloride

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

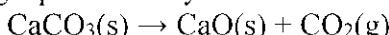
A **saturated solution of sodium chloride**, in contact with excess solid sodium chloride has two phase, namely aqueous solution and solid sodium chloride. The composition of both phase can be expressed in terms of two chemical individuals NaCl and H₂O.

Phase Components



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

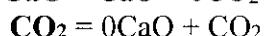
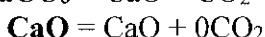
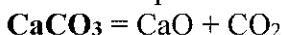
(4) **Decomposition of Calcium carbonate.** When calcium carbonate is heated in a closed vessel, the following equilibrium system results.



It has three phases: Calcium carbonate(s), Calcium oxide (s), and Carbon dioxide(g). The composition of all the phase can be expressed in terms of any two of the three chemical substances in equilibrium.

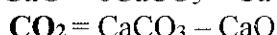
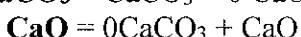
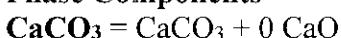
Let us select calcium oxide (CaO) and carbon dioxide (CO₂) as the components. Then we can write,

Phase Components



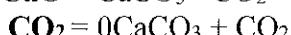
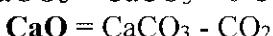
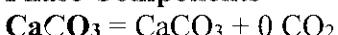
Again, selecting calcium carbonate (CaCO₃) and calcium oxide (CaO) as the components, we have

Phase Components



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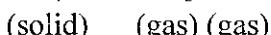
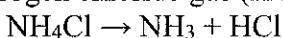
Phase Components



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

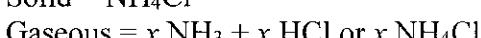
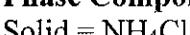
Furthermore, as is clear from the above examples, **by the components of a system is meant the number of chemical individuals and not any particular chemical substances by name.**

(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.

Phase Components



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

3.1.3. 'Degrees Of Freedom'

The term **Degree of Freedom** represented by F in the phase Rule equation ($F = C - P + 2$) is defined as: **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 **non-variant** or having no degree of freedom.

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

A system with $F = 2$ is known as **bi variant** 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.

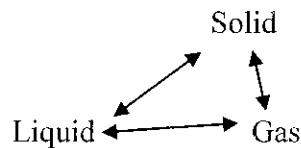
- (1) **For a pure gas, $F = 2$.** For a given sample of any pure gas $PV = RT$. If the values of pressure (P) and temperature (T) be specified, volume (V) can have only one definite value, or that the volume (the third variable) is fixed automatically. Any other sample of the gas under the same pressure 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 \leftrightarrow temperature only is 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 \leftrightarrow 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.
$$\text{NaCl} \leftrightarrow \text{NaCl-solution} \leftrightarrow \text{water vapour}$$

(solid)
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 ice \leftrightarrow water \leftrightarrow 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 ($F = 0$).**

3.1.4. Phase Reactions- Certain physical or chemical changes are associated with appearance or disappearance of phase. Such changes are called **Phase reactions**.

Examples –

- i) Change of solid to liquid – Melting
- ii) Change of liquid to solid – Freezing
- iii) Change of liquid to gas – Vaporisation
- iv) Change of solid to gas – Sublimation
- v) Change of gas to liquid – Condensation





All chemical changes may not be termed as phase reaction. Example – Gaseous H₂ and Cl₂ gives gaseous HCl, i.e. no change in phase.

3.1.5. Equilibrium Conditions:

The equilibrium among different phases is of three types and will exist under certain conditions as stated below-

- Thermal Equilibrium** – It means that temperature of all phases involved in equilibrium must be same, otherwise heat will flow from one phase to other in order to equalise thermal gradient.
- Mechanical Equilibrium** - It means that pressure on all phases involved in equilibrium must be same, otherwise one phase will expand in volume compared to other under high pressure.
- Chemical equilibrium** – Chemical potential of any component must be same in all phases that are in equilibrium, otherwise there will be development of concentration gradient.

★ 3.1.6. Advantages of Phase Rule (Merits)

- It provides simple method of classifying equilibrium states of system.
- It confirms that different systems having same degrees of freedom behave in similar manner.
- It predicts behaviour of system towards changes in temperature, pressure and composition.
- It is applicable to both physical and chemical phase reactions.
- It does not consider nature of reactant or product during phase reaction
- It predicts number of phases remaining or not remaining in equilibrium when transformed in other substance.

★ 3.1.7. Limitations (De merits)

- Not applicable to systems acquiring equilibrium slowly
- Applicable to single equilibrium state at a time. Does not tell about the number of other possible equilibria that are possible in system.
- It does not consider influence of Electric and Magnetic field on equilibrium.
- All phases in system must be at same temperature and pressure.

3.2. One Component System

3.2.1. 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 H₂O and hence one component 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 Figure.

3phase | 1 component

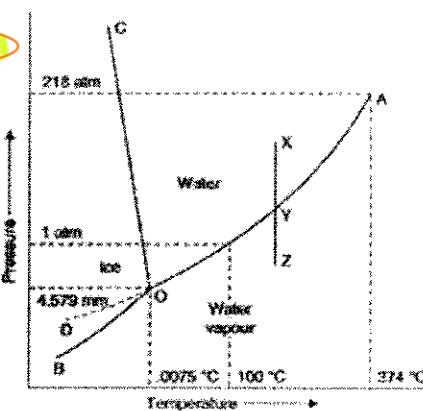


Fig. 11.1 The phase-diagram for water (not to scale).

The phase diagram consists of following features

- (1) Three stable 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 starts at point O and ends at point A . 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. It starts at point O and ends at point B . 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.

Curve OC , the Fusion curve of Ice- It starts at point O and ends at point C . 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**.

$$M.P. \text{ ice} \propto \frac{1}{P}$$

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**.

each of these two phase system has $F = 1$
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 **non variant**. 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**.

$$F = 2$$

★ (4) Metastable system: Super cooled 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 super cooled 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.

3.2.2. Sulphur System

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, $95.6^\circ\text{C} \ \alpha\text{-Sulphur} \leftrightarrow \beta\text{-Sulphur}$, 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, White phosphorus \longrightarrow Red 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 $S\mu$, $S\pi$ and $S\lambda$.



These three forms of sulphur differ in molecular structure. $S\lambda$ is S_8 , $S\pi$ is S_4 while formula of $S\mu$ is not known. The composition of the equilibrium mixture at 120°C and 444.6°C (b.p. of sulphur) is: $120^\circ\text{C} \ S\mu \ 0\% \ S\pi \ 3.7\% \ S\lambda \ 96.3\% \ 444.6^\circ\text{C} \ S\mu \ 37\% \ S\pi \ 4\% \ S\lambda \ 59\%$

Sulphur System –

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

(a) Two solid polymorphic forms:

(i) Rhombic Sulphur (SR)

(ii) Monoclinic Sulphur (SM)

Solid \leftarrow (b) Sulphur Liquid (SL)

Liquid \leftarrow (c) Sulphur Vapour (SV)

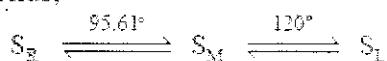
Gas(Vapour) \leftarrow All the four phase can be represented by the only chemical individual ‘sulphur’ (S) itself and hence one component of the system.

4 phase

1 component

The two crystalline forms of sulphur SR and SM exhibit enantiotropy with a transition point at 95.6°C. Below this temperature SR is stable, while above it SM 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, SM melts.

Thus,

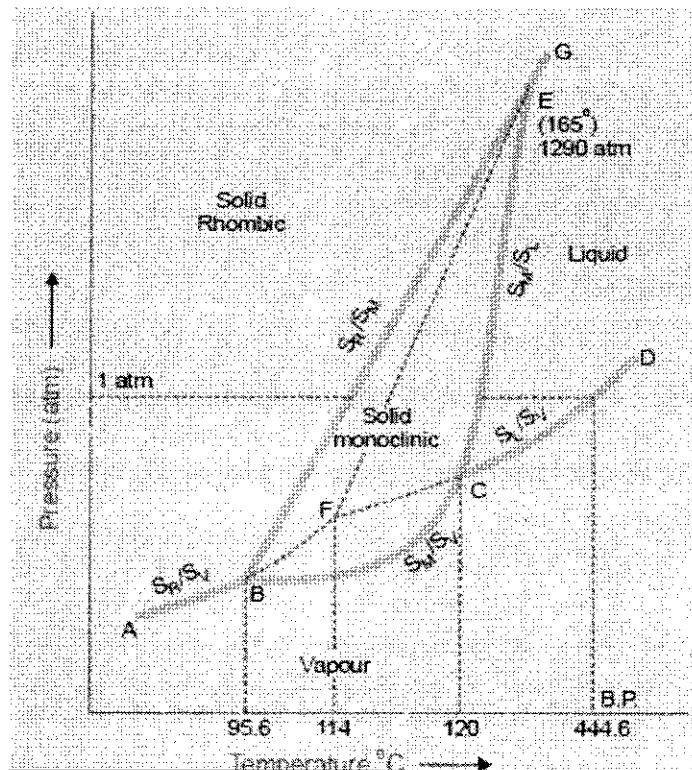


The phase diagram for the sulphur system is shown in Figure. The salient features of the phase diagram are described below.

- (i) There are six stable curves AB , BC , CD , BE , CE , EG
- (ii) There are three stable Triple points B , C , E
- (iii) The four distinct areas:
 ABG marked 'solid Rhombic'
 BEC marked 'solid Monoclinic'
 $GECD$ marked 'liquid Sulphur'
 $ABCD$ marked 'Sulphur vapour'
- (iv) Three metastable curves and one metastable triple point.

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

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



3 stable T. point

 1 metastable T. point
 Total 4

Sulphur system – Phase Diagram

Curve AB , the Vapour Pressure curve of SR. It shows the vapour pressure of solid rhombic sulphur (SR) at different temperatures. Along this curve the two phases SR and sulphur vapour (SV) are in equilibrium. The system SR/SV has one degree of freedom, $F = C - P + 2 = 1 - 2 + 2 = 1$ i.e., it is *monovariant*.

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

Curve CD , the Vapour Pressure curve of SL. It depicts the variation of the vapour pressure of liquid sulphur (SL) with temperature. SL and SV are in equilibrium along CD .

The two phase system SL/SV 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 SR and SM. As two solid phases are in **equilibrium** along the curve, the system SR/SM is **monovariant**. The transformation of SR and SM is accompanied by increase of volume (density of SR = 2.04; SM = 1.9) 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 SM. It represents the effect of pressure on the melting point of SM. The two phases in equilibrium along this curve are **SM** and **SL**. The system SM/SL is **monovariant**. As the melting or fusion of SM 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 SM ceases to exist beyond this point.

Curve EG, the Fusion curve for SR. Here the two phases in equilibrium are **SR** and **SL**. The number of phases being two, the system SR/SL 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 SR, solid SM and SV are in **equilibrium** at the point *B*. There being three phases and one component, the system SR/SM/SL is **non variant**.

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

At *B*, SR is changed to SM 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 **SM**, **SL** and **SV**. There being three phases and one component, the system **SM/SL/SV** is **nonvariant**. The temperature corresponding to *C* as indicated on the phase diagram is 120°C. This is the **melting point of SM**.

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 **SR**, **SM** and **SL** are in **equilibrium** and the system at the point *E* is **non variant**. This point gives the conditions of existence of the system SR/SM/SL 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 **SR**, **SM**, **SL**, and **SV** are **bivariant**.

4 regions
for each $F=2$

★ (4) Metastable Equilibria

The change of SR to SM takes place very slowly. If enough time for the change is not allowed and SR is heated rapidly; it is possible to pass well above the transition point without getting SM. In that case, there being three phases (SR, SL, SV) 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 SR. This is a continuation of the vapour pressure curve *AB* of stable SR. The metastable phases SR and SV are in equilibrium along this curve. It is a **monovariant system**.

The dashed curve CF, the Vapour Pressure curve of super cooled SL. On super cooling 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 super cooled SL and SV. Thus

it may be designated as the vapour pressure curve of super cooled SL. It meets the dashed curve BF at F .

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

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

3.3. 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 have 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

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

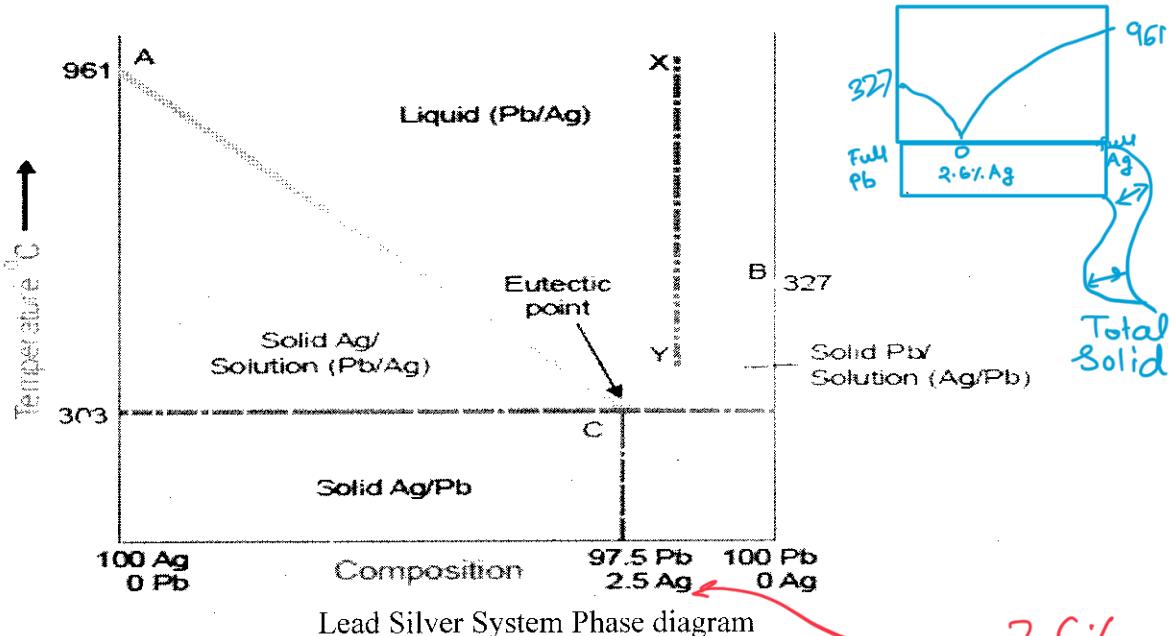
Where F' gives the remaining degrees of freedom of the system. The reduced phase rule is more convenient to apply to solid/liquid two-component condensed system. Since the only variables for two-component solid/liquid systems are temperature and composition, the phase diagrams for such systems consist of Temperature-Concentration graphs (*TC graphs*).



3.3.1. The Lead - Silver 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 figure.





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 A ; 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 $\text{Ag}/\text{solution}$ 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 $\text{Ag}/\text{Pb}/\text{solution}$ at C is *non variant*. Both the variables, temperature (303°C) and composition ($97.5\% \text{ Pb}, 2.5\% \text{ Ag}$) 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 non-existent.

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 *bi variant*.

The area below AC represents the phases $\text{Ag} + \text{solution}$, while that below BC the phases $\text{Pb} + \text{solution}$. The area below the temperature 303°C , represents solid $\text{Ag} + \text{solid Pb}$. 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 Argentiferrous Lead Application

This process of recovery of silver from argentiferrous lead is based on the facts contained in the phase diagram (Fig.). The argentiferrous 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

97.4%
& 2.6%

Correction

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.

★ 3.3.2 Applications of simple eutectic systems

- a) A mixture of 23.3% NaCl and balance ice has lowest temperature attained by freezing mixture (-21.2°C)
- b) Eutectic alloys of Na and K are used as coolant in nuclear reactors.
- c) Eutectic alloys of Pb and Sn are used as solders.
- d) Eutectic alloys are used in inks / toners for copiers and printers
- e) Low melting eutectic alloys are used for safety valves in cooker, boiler, automobiles etc.
- f) Au and Si eutectics are used in electronic industry.
- g) Wood and Field's metals are used in fire sprinklers.
- h) Knowledge of eutectic point is essential in foundry industry.

Questions

Answer the following

1. State Gibb's phase rule and explain with different examples the terms involved there in.
2. What are phase reactions? Explain why all chemical reaction are not phase reactions.
3. Which types of equilibriums are associated with heterogeneous system? Mention equilibrium conditions for each type.
4. List merits and demerits (advantages/ disadvantages) of phase rule.
5. With neat labelled diagram discuss Water system.
6. With neat labelled diagram discuss Sulphur system.
7. With neat labelled diagram discuss Pb-Ag system.
8. Discuss de-silverization of Argentiferous Lead by Pattinson's process.
9. What is reduce phase rule? Why two component system uses reduce phase rule.
10. List applications of Eutectic system.

Define following terms

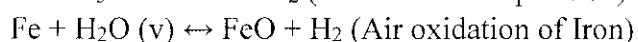
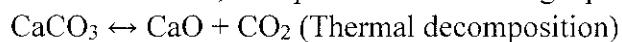
Phase, Component, Degree of freedom, Phase reaction, Triple point, Eutectic point, Metastable state, Polymorphism, Enantiotropy, Monotropy

Give reason

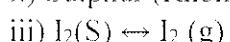
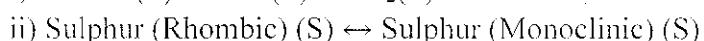
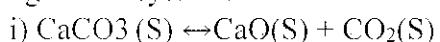
1. Mixture of any number of phases constitutes one phase.
2. System along any curve is mono variant.
3. System at triple point is non variant.
4. Transition curve in sulphur system is incline towards right.
5. Water and sulphur system is one component system but water system consist one triple point and sulphur system consist three triple points.
6. Phase diagram of Lead-silver system is T-C Curve and not T-P Curve.
7. Water and sulphur are one component system.
8. System in any area is bi variant.
9. Phase rule is not applicable to system acquiring equilibrium slowly.
10. Phase rule can predict regarding only one equilibrium state at a time.

Determine Phases/ Component / degree of freedom.

1. Calculate & List Phases, Components of following equilibria.



2. Calculate number of Component and name of component present in the following heterogeneous systems.



3. Determine number of Phases, Components and Degrees of freedom for following

i) Aqueous NaCl solution.

ii) Aqueous sodium chloride solution containing undissolved solid in equilibrium with water vapour.

iii) Ice, Liquid water and water vapour in equilibrium.