PHASE RULE

By:

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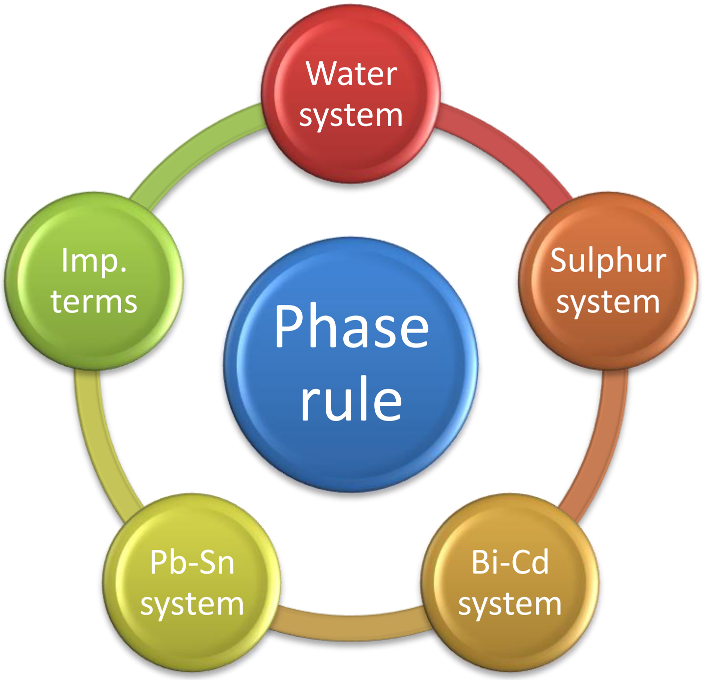

Introduction

The term phase rule was first introduced by Willard Gibbs in 1876. According to him, in a homogeneous system in equilibrium; the number of degree of freedom is greater than the difference between the number of components and number of phases by 2.

Mathematically, $\boxed{F = C - P + 2}$

Where, F = Number of degree of freedom, C = Number of components, P = Number of phases

System

A system may consist of a substance, or a number of substances, which are completely isolated from the surroundings. The substances present in it are free to react only with each other and subjected to change their composition, temperature, pressure or volume.

Phase

It is defined as a homogeneous and physically distinct part of a system which is separated from other such parts of the system by means of definite boundary. Hence simply we can say phase is a physically-distinct, chemically-homogeneous and mechanically-separable region of a system. For example: a gas, mixture of gases, two miscible liquids are the examples of a single phase.

Example-1

In water system, three phases are there. i.e., ice (solid), water (liquid) and vapour (gas) are in equilibrium and separated by definite boundary surfaces.

$$\text{Ice}(\text{solid}) \rightleftharpoons \text{Water}(\text{liquid}) \rightleftharpoons \text{Vapour}(\text{gas})$$

Example-2

A gaseous system always consists of a single phase as the gases are miscible and forms homogeneous mixture.

Example-3

In case of liquid solutions, there are two possible cases one is for miscible liquids and other is for immiscible liquids.

Case-I:

In case of miscible liquids, the liquids are totally mixed in all proportion. So, only one phase is there. If two liquids are miscible, than there is only one phase.

For example: mixture of alcohol and water, only one phase.

Case-II:

If two liquids are immiscible, than there are two layers. For example: mixture of benzene and water, there are two phases separated by a definite boundary. Similarly, if three liquids are immiscible, than there are three phases.

Component

It is defined as the smallest number of individual constituents by means of which the composition of each phase can be described either directly or in terms of chemical equation. Simply we can say a component is a chemically independent constituent of a system.

Example-1

Any system having single chemical individual is one component system. For example, water system consists three phases, i.e., ice (solid), water (liquid) and vapour (gas), which is in equilibrium.

$$\text{Ice}(\text{solid}) \rightleftharpoons \text{Water}(\text{liquid}) \rightleftharpoons \text{Vapour}(\text{gas})$$

The composition of each of the three phases can be expressed in terms of the component H_2O. So it is one component system.

Example-2

The sulphur system consists four phases (rhombic, monoclinic, liquid and vapour). Since each form can be expressed in terms of only sulphur, so it is one component system.

Degree of Freedom (F)

It is the minimum number of independently variable factors such as temperature, pressure and composition which are required to define the system completely (without disturbing the number of phases in equilibrium). The systems possessing zero, one, two and three degree of freedoms are called invariant, uni-variant, bi-variant and tri-variant respectively.

We know, $F = C – P + 2$

Where, F = Degree of freedom, C = Component, P = Phase.

Example-1

Consider a one component system having three phases.

$$\text{Ice}(\text{solid}) \rightleftharpoons \text{Water}(\text{liquid}) \rightleftharpoons \text{Vapour}(\text{gas})$$

Here the three phases are in equilibrium at one particular temperature and pressure. If temperature or pressure is altered, then the three phases will not remain in equilibrium and one of the phases disappears. Hence there is no independent variable. So $F = 0$ and the system is non-variant or invariant.

Example-2

If the system consists two phases such as water and vapour, in equilibrium -

$$\text{Water}(l) \rightleftharpoons \text{Vapour}(g)$$

Either temperature or pressure is sufficient to define the system completely, i.e., if we fix one variable ‘T’ then the other variable ‘P’ is automatically fixed. If temperature or pressure is altered, then the two phases will not remain in equilibrium. So, $F = 1$ and the system is uni-variant.

Derivation of phase rule

Consider a system of P phases and C components. We know for each component, there are P concentration variables. So for C components, there are CP concentration variables. In addition to this, two external variables are pressure and temperature. Hence total number of variables is $CP + 2$.

Again, for each phase there is one equation of state. So for P phases there are P phase equations. Since for P phases, we have $(P - 1)$ chemical potential equations. As there are C components, so we have $C (P - 1)$ chemical potential equations. Hence total number of equations $= P + C (P - 1)$

$$F = \text{Total number of variables} - \text{Total number of equations}$$

$$= CP + 2 - [P + C (P - 1)]$$

$$= CP + 2 - P - CP + C$$

$$\Rightarrow \boxed{F = C - P + 2}$$

One component system

It is a system in which the composition of all phases can be expressed in terms of only one substance. In one component system, C = 1

We know F = C – P + 2

∴ F = 1 – P + 2

⇒ F = 3 – P

Water system

Water mainly exists in three different phases such as ice (solid), water (liquid) and water vapour (gas).

$$\text{Ice}(\text{solid}) \rightleftharpoons \text{Water}(\text{liquid}) \rightleftharpoons \text{Vapour}(\text{gas})$$

Such phases lead to the following equilibria.

Two phase equilibria

Solid ↔ Liquid

Solid ↔ Track

Liquid ↔ Vapour

Three phase equilibria

Solid ↔ Liquid ↔ Vapour

The phase rule of water system can be represented graphically by considering temperature-pressure diagram as shown in Figure 1. The diagram consists of –

(i) Four curves (OA, OB, OC, OB')
(ii) Three areas (AOC, AOB, BOC)
(iii) Triple point (O)

Study of the curves

(b) Curve OA:

This curve is called sublimation curve as it gives the vapour pressure of solid ice in equilibrium with water vapour at different temperatures. This curve separates the solid ice from water vapour and explains how the two phases coexist in equilibrium. The OA curve starts from O (triple point) and terminates at A (absolute zero, -273 ^{o}C), beyond which no vapour exists. According to phase rule –

$$F = C - P + 2$$

$$= 1 - 2 + 2 = 1 \text{ (system is mono-variant)}$$

(a) Curve OB:

This curve is called vapour pressure curve or vaporization curve as it gives the vapour pressure of liquid water in equilibrium with water vapour at different temperatures. The vapour pressure increases with the rise in temperature. This curve separates the liquid from vapour and explains how the two phases coexist in equilibrium. The OB curve starts from O (triple point) and terminates at B (critical point, 374 ^{o}C, 218 atm). According to phase rule –

$$F = C - P + 2$$

$$= 1 - 2 + 2 = 1 \text{ (system is mono-variant)}$$

(c) Curve OC:

This curve is called freezing point curve or fusion curve as it tells how the freezing temperature of water (melting temperature of ice) varies with pressure. This curve separates the solid ice from liquid water and explains how the two phases coexist in equilibrium. The OC curve starts from O (triple point) and terminates at C (very high pressure). This indicates that melting point of ice is lowered with the increase in pressure. According to phase rule –

$$F = C - P + 2$$

$$= 1 - 2 + 2 = 1 \text{ (system is mono-variant)}$$

(d) Curve OB' (Metastable curve):

Equilibrium which can be attended in only one direction is known as metastable equilibrium. The doted curve OB' is a continuous extension of BO curve. It is obtained when liquid water is super cooled, i.e., cooling of liquid water below the freezing point without the separation of solids. Here water and vapour are in metastable (unstable) equilibrium. As it is unstable, the super cooled liquid will be immediately converted into ice by slight disturbance of equilibrium. The degree of freedom is one. Hence the system is also mono-variant.

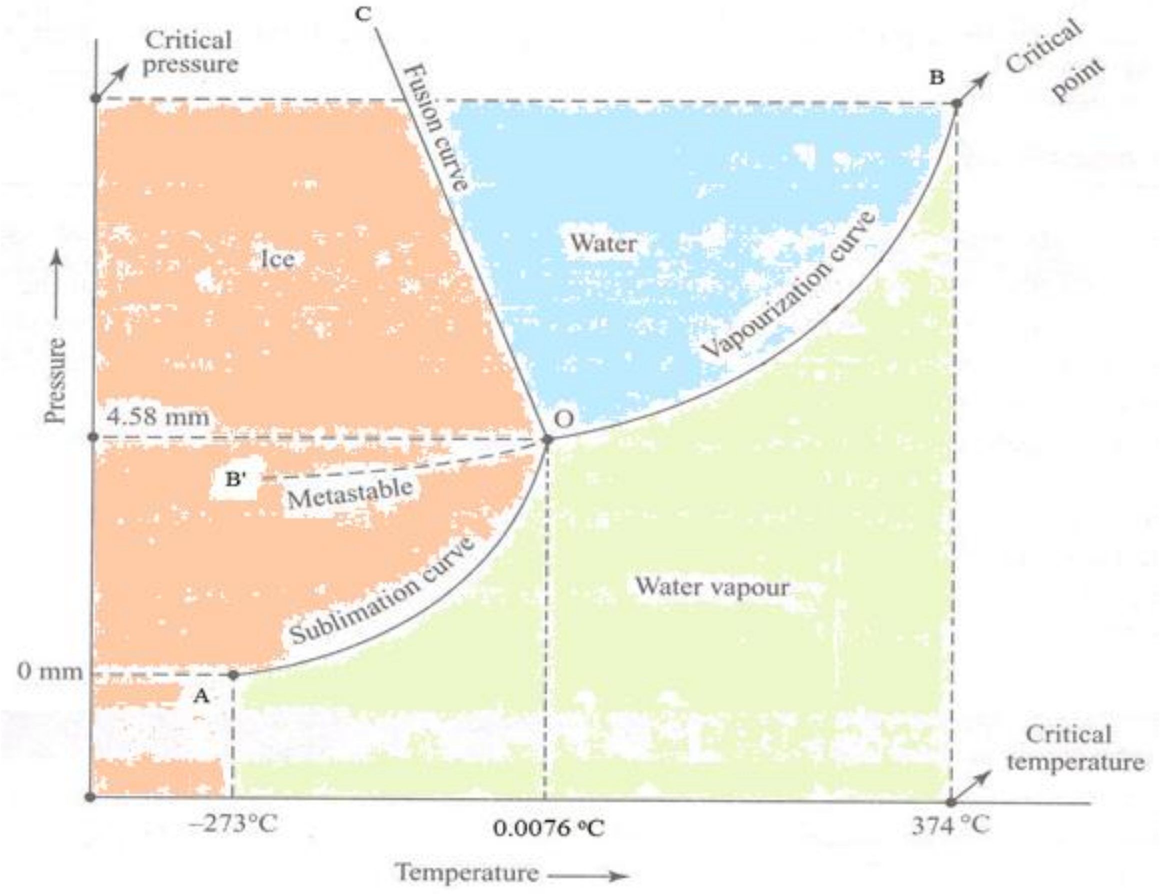

Figure 1. The phase diagram of water system

Study of the areas

The phase diagram is divided into three areas, namely AOC, AOB and BOC for the regions ice, vapour and water respectively. One phase is present in each area. According to phase rule –

F = C – P + 2

= 1 – 1 + 2

= 2 (Bi-variant in nature)

This means both temperature and pressure are required to define the system completely at any point within the area.

Triple point

The curves OA, OB and OC meet at this point where all the three phases are in equilibrium. The temperature and pressure corresponding to this equilibrium are 0.0076 ^{o}C and 4.58 mm Hg respectively. According to phase rule –

F = C – P + 2

= 1 – 3 + 2

= 0 (In-variant in nature)

The three phases can coexist in equilibrium only under one set of conditions. i.e., if any of the two variables is slightly changed, the equilibrium is not exist and one of the phases would disappear.

Sulphur system

Sulphur mainly exists in four different phases (two solid, one liquid and one vapour) namely rhombic (S_R), monoclinic (S_M), liquid (S_L) and vapour (S_V) phases. So sulphur system is a one component and four phase system. Such phases lead to the following equilibria.

Two phase equilibria

$S_R \leftrightarrow S_M$

$S_R \leftrightarrow S_L$

$S_R \leftrightarrow S_V$

$S_M \leftrightarrow S_V$

$S_M \leftrightarrow S_L$

$S_L \leftrightarrow S_V$

Three phase equilibria

$S_R \leftrightarrow S_M \leftrightarrow S_V$

$S_R \leftrightarrow S_L \leftrightarrow S_V$

$S_R \leftrightarrow S_M \leftrightarrow S_L$

$S_M \leftrightarrow S_L \leftrightarrow S_V$

Four phase equilibria

$S_R \leftrightarrow S_M \leftrightarrow S_L \leftrightarrow S_V$

Let all the four phases in sulphur coexist in equilibrium. Applying phase rule –

$F = C – P + 2$

$= 1 – 4 + 2$

$= -1$ (impossible)

Hence all the four phases in sulphur system can not coexist at the same time. The phase rule of sulphur system can be represented graphically by considering temperature-pressure diagram as shown in Figure 2. The diagram consists of –

(i) Six curves (AB, BC, CD, BF, CF, FG)
(ii) Four areas (ABCD, ABFG, DCFG, BCF)
(iii) Triple points (B, C, F)

(iv) Metastable curves (BE, CE, CF)

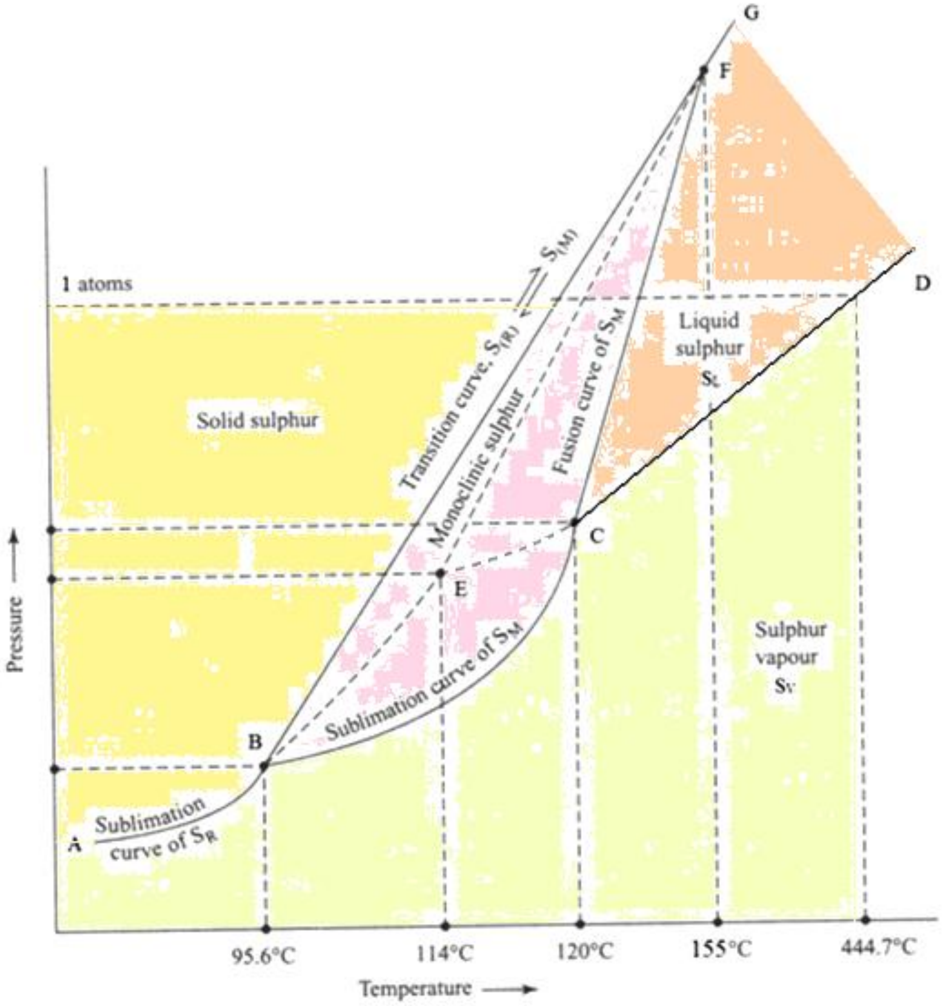

Figure 2. The phase diagram of sulphur system

Study of the curves

(a) Curve AB:

This curve is called sublimation curve of rhombic sulphur and gives the vapour pressure of rhombic sulphur at different temperatures. This curve explains how the two phases rhombic sulphur and vapour sulphur coexist in equilibrium. According to phase rule –

$F = C - P + 2$

$= 1 - 2 + 2$

= 1 (monovariant)

(b) Curve BC:

This curve is called sublimation curve of monoclinic sulphur and gives the vapour pressure of monoclinic sulphur at different temperatures. This curve explains how the two phases monoclinic sulphur and vapour sulphur coexist in equilibrium. The system is monovariant.

(c) Curve CD:

This curve is called vapour pressure curve of liquid sulphur and gives the vapour pressure of liquid sulphur at different temperatures. This curve explains how the two phases liquid and vapour sulphur coexist in equilibrium. The system is monovariant.

(d) Curve BF:

This curve is called transition curve and gives the effect of pressure on the transition temperature of rhombic sulphur into monoclinic sulphur. This curve explains how the two phases rhombic sulphur and monoclinic sulphur coexist in equilibrium. The system is monovariant.

(e) Curve CF:

This curve is called fusion curve of monoclinic sulphur and gives the effect of pressure on the melting point of monoclinic sulphur. This curve explains how the two phases monoclinic sulphur and liquid sulphur coexist in equilibrium. The system is monovariant.

(f) Curve FG:

This curve is called fusion curve of rhombic sulphur and gives the effect of pressure on the melting point of rhombic sulphur. This curve explains how the two phases rhombic sulphur and liquid sulphur coexist in equilibrium. The system is monovariant.

Study of the areas

The phase diagram is divided into four areas, namely ABCD, ABFG, DCFG and BCF for the regions vapour sulphur, rhombic sulphur, liquid sulphur and monoclinic sulphur respectively. One phase is present in each area. According to phase rule –

$F = C - P + 2$

$= 1 - 1 + 2$

$= 2$ (Bi-variant in nature)

This means both temperature and pressure are required to define the system completely at any point within the area.

Triple points

The various triple points are as follows –

(i) Point B

The point B represents the transition temperature (95.6 ^{o}C) at which rhombic sulphur is changed into monoclinic sulphur. The three phases coexist in equilibrium at this point are $S_R \leftrightarrow S_M \leftrightarrow S_V$. According to phase rule –

$F = C - P + 2$

= 1 – 3 + 2

= 0 (Invariant in nature)

(ii) Point C

The point C represents the melting point (120 ^{o}C) of monoclinic sulphur. The three phases coexist in equilibrium at this point are $S_M \leftrightarrow S_L \leftrightarrow S_V$. According to phase rule –

F = C – P + 2

= 1 – 3 + 2

= 0 (Invariant in nature)

(iii) Point F

The point F represents the conditions of existence of the systems (S_R/S_M/S_L) at 155 ^{o}C temperature and 1290 atm pressure. The three phases coexist in equilibrium at this point are $S_R \leftrightarrow S_M \leftrightarrow S_L$. According to phase rule –

F = C – P + 2

= 1 – 3 + 2

= 0 (Invariant in nature)

Metastable curves (BE, CE, EF)

Curve BE

This curve is a continuous extension of AB and represents metastable equilibria of $S_R \leftrightarrow S_V$. The system is monovariant.

Curve CE

This curve is a continuous extension of DC and represents metastable equilibria of $S_L \leftrightarrow S_V$. The system is monovariant.

Curve EF

This curve is a continuous extension of FG and represents metastable equilibria of $S_R \leftrightarrow S_L$. The system is monovariant.

Metastable triple point

The point E represents the metastable triple point of three metastable phases (S_R, S_L and S_V). The three phases coexist in equilibrium at this point are $S_R \leftrightarrow S_L \leftrightarrow S_V$. The system is invariant.

Two component system

In a two component system, C = 2. According to phase rule –

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - P + 2 \\ &= 4 - P \end{aligned}$$

The minimum number of phases in a two component system is one. So the maximum number of degree of freedom is –

$$\begin{aligned} F &= 4 - P \\ &= 4 - 1 \\ &= 3 \end{aligned}$$

This means all the three variables (pressure, temperature and concentration) must be specified in order to describe a two component system completely. For the graphic representation of these variables, a three dimensional diagram is required in which the three co-ordinate axes representing pressure, temperature and concentration are at right angles to each other. But phase equilibria is mainly deal with 2D diagram. So, one of the variables is kept constant. The possible equilibria in a two component system are –

(i) Solid ↔ Liquid
(ii) Solid ↔ Gas
(iii) Liquid ↔ Liquid
(iv) Liquid ↔ Gas

In a Solid ↔ Liquid equilibria, the gas phase is absent. So pressure variable is kept constant. Such system is called condensed system. The phase rule will be reduced by 1.

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

It is known as **reduced phase rule** equation. As the two variables are temperature and composition, the phase diagram for two component systems (Solid ↔ Liquid equilibria) are represented by temperature-concentration (TC) graphs.

Eutectic system

A binary system consisting of two substances which are miscible in all proportion in the liquid phase but do not react chemically is known as eutectic system. Simply we can say the systems that possess eutectic point are called eutectic systems. For example: Mixture of lead and silver. The phase diagram of eutectic system is shown in Figure 3.

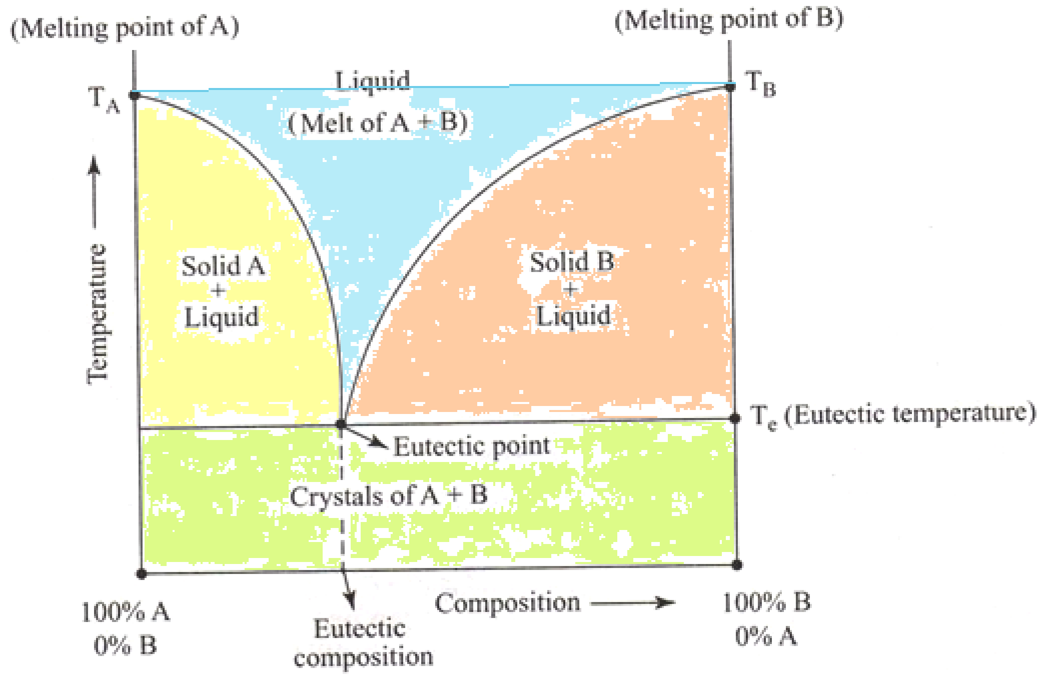

Figure 3. Phase diagram of eutectic system

These two curves represent the two phase equilibria. By applying reduced phase rule equation –

$$F = C - P + 1$$

$$= 2 - 2 + 1$$

$$= 1 \text{ (Monovariant)}$$

The eutectic systems are used in the preparation of low melting alloys such as solders.

Eutectic mixture

It is a solid solution of two or more substances having lowest freezing point of all possible mixtures of the components. For example: mixture of lead and silver.

Eutectic point

Two or more solid substances capable of forming of solid solution of each other have the property of lowering each of the freezing points attendable corresponding to the eutectic mixture is called as eutectic point. Simply we can say it is the point at which the liquidus line and the solidus line meet.

Eutectic composition

The composition corresponding to eutectic point is called eutectic composition.

Eutectic temperature

The temperature corresponding to eutectic point is called eutectic temperature. The eutectic temperature is lower than the melting point of either of the two metals. i.e., below eutectic temperature, no liquid phase of any composition can exist in the system.

Eutectic reaction

The process of phase change at the eutectic point is called eutectic reaction.

Bismuth-Cadmium (Bi-Cd) system

It is a two component and four phase system. The various phases are as follows.

(i) Solid bismuth
(ii) Solid cadmium
(iii) Solution of molten Bi and Cd
(iv) Vapour

The vapour phase is practically absent because the boiling points of Bi and Cd are very high. So it is a condensed three phase system. Here pressure has no effect on the system. Hence two remaining variables (temperature and concentration) are required to describe the system completely. The TC diagram is shown in Figure 4.

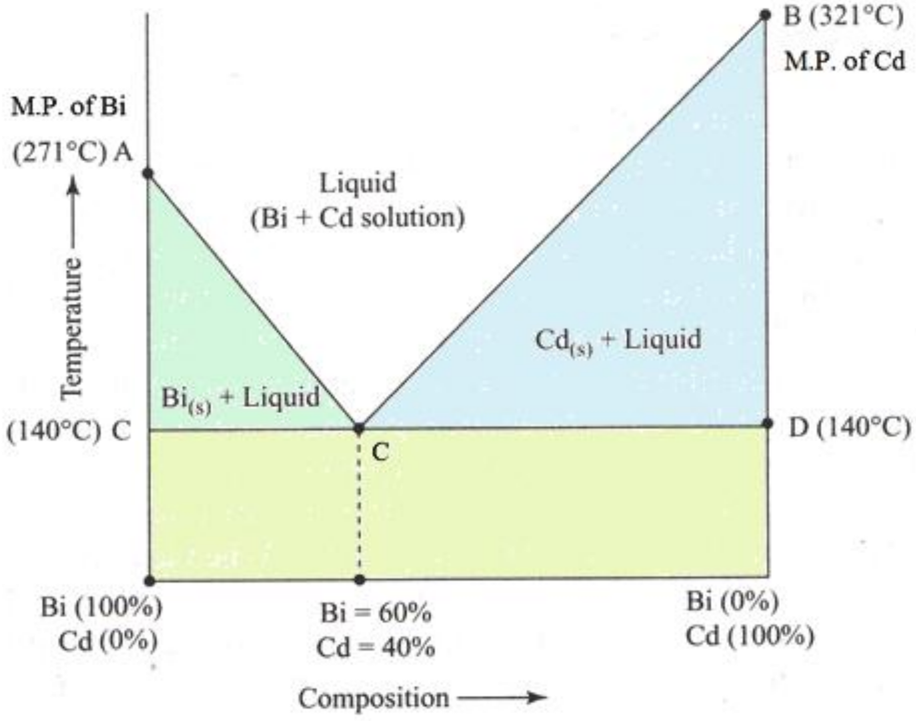

Figure 4. Phase diagram of Bi-Cd system

The diagram consists of –

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

Curve AC

It is the freezing point curve of Bi and shows how the melting point is lowered by the addition of Cd. Point A represents the freezing point or melting point (271 ^{o}C) of solid Bi. Here the two phases solid Bi and solution (Bi and Cd) are in equilibrium. According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 2 + 1

= 1 (monovariant)

Curve BC

It is the freezing point curve of Cd and shows how the melting point is lowered by the addition of Bi. Point B represents the freezing point or melting point (321 ^{o}C) of solid Cd. Here the two phases solid Cd and solution (Bi and Cd) are in equilibrium. According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 2 + 1

= 1 (monovariant)

Eutectic point (C)

Eutectic point C is the intersect of AC and BC. Here the three phases solid Bi, solid Cd and solution (Bi and Cd) are in equilibrium. According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 3 + 1

= 0 (Invariant)

The eutectic temperature is 140 ^{o}C and the eutectic composition is 60% (Bi) and 40% (Cd).

Area above ACB

It represents a single phase system (solution of Bi and Cd). According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 1 + 1

= 2 (bivariant)

Area below AC

It represents a two phase system (i.e., solid Bi and solution are in equilibrium). According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 2 + 1

= 1 (mono-variant)

Area below BC

It represents a two phase system (i.e., solid Cd and solution are in equilibrium). According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 2 + 1

= 1 (mono-variant)

The area below 140 ^{o}C, represents a two phase system (solid Bi and solid Cd). According to reduced phase rule equation –

F’ = C – P + 1

= 2 – 2 + 1

= 1 (mono-variant)

Lead-Tin (Pb-Sn) system

The phase diagram of Pb-Sn system is shown in Figure 5. In the Pb-Sn system, there are two components (namely, Pb and Sn), So, C = 2.

At fixed pressure, F = C–P+1. In the melt phase, P = 1, (practically no vapor phase exist), therefore, F = 2. The pressure is fixed, the composition and the temperature can change free.

At the liquidus curves, P = 2, C = 2, so, F = 1. The pressure is fixed, temperature or composition could change.

At the eutectic point all three phases, that is liquid, solid A (α) and solid B (β), exist in equilibrium, P = 3, C = 2, so F = 0. The pressure is fixed, therefore neither the temperature nor the composition can change free. ***The eutectic is the only point on the diagram where this is true.*** The phase diagram of lead and tin (Figure 5&6) is very similar. If the lead content in the melt < 5 %, or > 80.5 % (weight percent) mixed crystallites α or β are formed.

Example- If a Pb-Sn alloy (Pb=70%, Sn=30%) is heated slowly from 160 ℃. At what temperature, the first liquid phase will form? Ans- At 183 ℃, first liquid phase will form.

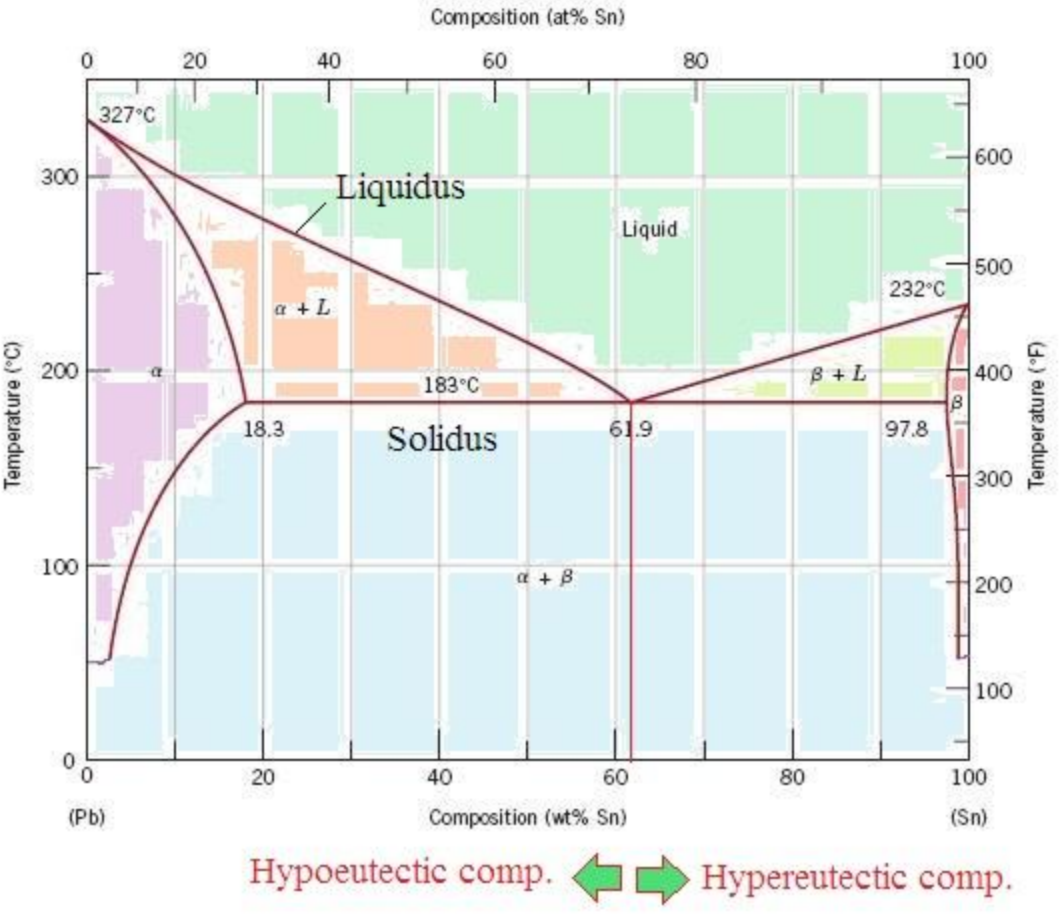

Figure 5. Phase diagram of Pb-Sn system

Traditionally, tin-lead mixtures have been used as solder, but these are being phased out due to health concerns. This is especially the case where the solder is used to join water pipes where the water is used for drinking. New non-lead solders have been developed as safer replacements. Ex- 60% tin and 40% lead. This is close to the eutectic composition (62% tin and 38% lead), giving a low melting point. It will also melt and freeze cleanly over a very limited temperature range. This is useful for electrical work.

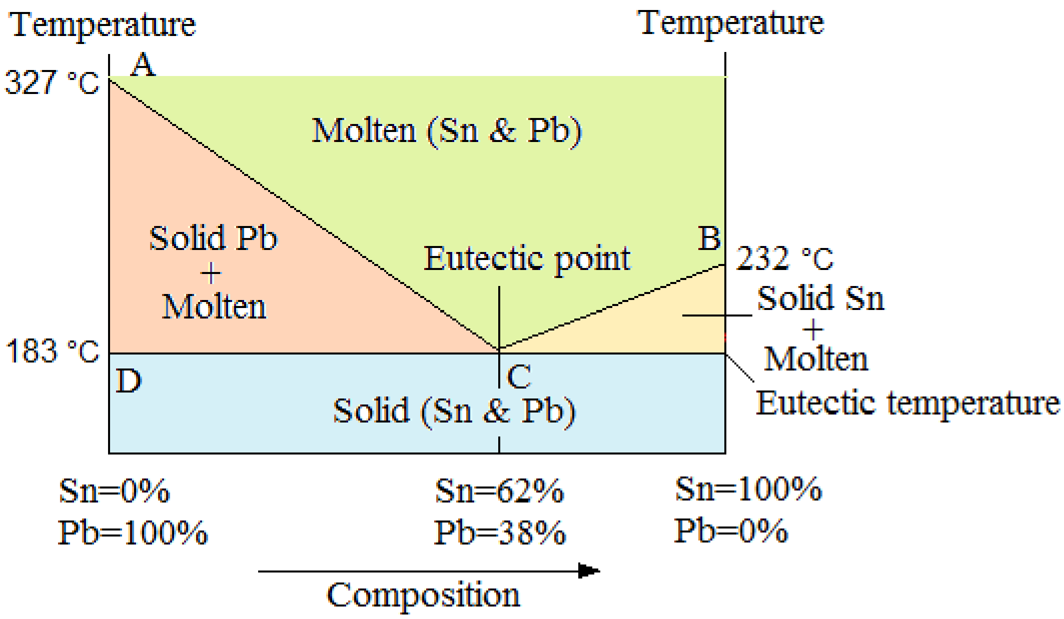

Figure 6. This is a simplified version of the actual lead-tin phase diagram. Here, the tin-lead axis is reversed. The two lines meeting at the eutectic point have been simplified slightly so that they are drawn as straight lines rather than slight curves. It doesn't affect the argument in any way.

Uses of phase rule

1. It gives a simple method to classify equilibrium states of systems.
2. The phase rule applies to both physical and chemical phase reactions.
3. By knowing degree of freedom and number of components, it is possible to predict the number of phases coexisting in the system under equilibrium.
4. It tells that different systems having same number of degrees of freedom behave in the same manner.
5. The phase rule is applicable to macroscopic systems. So it does not give the information about the molecular structure.
6. The phase rule gives the information about the behavior of the system.

7. It is very useful in metallurgical industries.

Limitations of phase rule

1. The phase rule is applicable to only the systems in equilibrium.
2. The phase rule takes into account only the variables, temperature, pressure and composition.
3. It cannot be applied to systems consisting two or more solutions separated by semi permeable membrane.
4. It is only applicable to single equilibrium state, so it does not tell about other possible equilibrium present in that system.

References (for further reading….)

1. Engineering Chemistry with Laboratory Experiments, R. K. Mohapatra, PHI, Delhi, 2015.
2. A Text book of Physical Chemistry, K. K. Sharma & L. K. Sharma, Vikas, New Delhi, 2014.
3. H. J. Fecht, M.-X. Zhang, Y. A. Chang & J. H. Perepezko, Metall. Trans. A, 20A (1989) 795-803.
4. T. L. Ngai & Y. A. Chang, CALPHAD, 5 (1981) 271-276.
5. I. Karakaya & W. T. Thompson, Bull. Alloy Phase Diagrams, 9 (1988) 144-152.
6. H. Ohtani, K. Okuda & K. Ishida, J. Phase Equilibria, 16 (1995) 416-429.

Thank you.