## PHASE RULE

It is a relationship for determining the least no. of intensive variables that can be changed without changing the equm of the system

It is a generalization given by J.W. Gibbs which seeks to explain the equilibria existing in heterogeneous systems provided the equilibria between any no. of phases is only influenced by T, P & composition but not by electrical field, gravity, magnetic field etc.

Mathematically, it can be written as

$F = C - P + 2$ where F = Degree of freedom of system

C = No. of components of system

P = No. of phases in the system

2 = ~~addita~~ Temp & pressure variables.

### Definition of Terms used

**Phase(P):** It is defined as a homogeneous, physically & mechanically separable distinct portion of a system, which is separated from other portion of a system by ~~bou~~ definite boundary surfaces. A phase may be gas, liquid or solid. It is important to understand that phase is not same as physical state. Physical state of a ~~system~~ substance means solid, liquid or gas. ~~A phase~~

**Examples:** ① All non-reacting gaseous mixture constitute one phase only

② Miscible liquids constitute one phase.

alcohol + water

③ In an immiscible liquid system, each layer is counted as a separate phase. oil + water

④ A solution of substance form one phase. sugar + water.

⑤ saturated solⁿ of a substance form two phase, i.e, solid solute & solⁿ.

⑥ Each solid constitute a separate phase except the case of solid solution. Ex. alloy, double salt like Mohr's salt ($(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$)

⑦ Each polymorphic form constitute one phase. ex. Sulfur exist in rhombic & monoclinic crystal form, which are different, hence constitute 2 phases.

~~Components (c)~~ Thermal decomposition of $CaCO_3$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad P = 3$$

$$NH_4Cl(s) \rightleftharpoons NH_3 + HCl(g) \qquad P = 2$$

Components (c): It can be defined as the minimum no. of chemically independent constituents of a system, by means of which, the composition of each phase can be expressed directly or in the form of chemical equation.

It should be noted that the term "constituents" is different from "components". Constituents means the no. of chemical species

present in the system but component means it is an independent constituent by means of which we can define a system. Every component must be a constituent but every constituent may not be a component.

The no. of components of a system is equal to the no. of constituents if there is no chemical rxn otherwise it is different. In latter case, the no. of components may be easily calculated from the no. of different chemical species (constituents) present minus the no. of chemical equations connecting them.

That is $C = N - E$

$N$ = Total No. of chemical species present

$E$ = No. of independent equations relating the chemical species.

Ex * In system, Ice ⇌ Water ⇌ Vapor.

$P = 3$, $C = 1$, i.e. $H_2O$.

* Sulfur system consists of 4 phases.

$S_R \rightleftharpoons S_M \rightleftharpoons S_L \rightleftharpoons S_V$ and can be expressed in terms of the single constituent – Sulfur. So $C =$

* A system in which thermal decomposition of $CaCO_3$ takes place in a closed container obeys equ$^n$ $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

consists of 3 phases & the no. of constituents is 3.
But these 3 constituents are not chemically independent and are related through the chemical eqn.
Any two constituents may be chosen as components to express the composition of all three phases. Hence it is a 2 component system.

Let's say CaO & $CO_2$ are components.

$$CaCO_3 = CaO + CO_2, \quad CaO = CaO + 0\,CO_2$$
$$CO_2 = 0\,CaO + CO_2$$

$$\boxed{C = N - E = 3 - 1 = 2}$$

* The decomposition of $NH_4Cl$ in a closed container is given acc. to the eqn

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}.$$

The system consists of two phases & three ~~const~~ chemical species. Since the proportion of $NH_3$ & HCl is same in the gaseous mixture ~~of $NH_3$ & HCl~~ as it is in the solid $NH_4Cl$ i.e. the ratio of $NH_{3(g)} : HCl_{(g)} = 1:1$ fixed. all the phases can be expressed by the same chemical formula, i.e. $NH_4Cl$. Hence this system is a one component system. $\boxed{C = N - E = 3 - 2 = 1}$

If an excess of $NH_3$ or HCl is added to the system, the no. of components increases to 2, bcoz the vapor phase has no longer the same composition as the solid $NH_4Cl$. that means $NH_{3(g)} \neq HCl_{(g)}$

* The system, decomposition of $PCl_5$ in closed container as per eqn

$$PCl_{5(s)} \rightleftharpoons PCl_{3(l)} + Cl_{2(g)}$$

consists of 3 phases & 3 chemical species. But these constituents are ~~independent~~ not chemically independent & are related through the chemical equ$^n$.

Hence $\boxed{C = N - E = 3 - 1 = 2}$

* $CaSO_4$ dissociates on heating in vacuum as per the equ$^n$ $2CaSO_{4(s)} \rightleftharpoons 2CaO_{(s)} + 2SO_{2(g)} + O_{2(g)}$

The no. of phases present is 3 (2 solids & 1 gas). The no. of chemical species present is 4. There is one chemical equ$^n$ relating these constituents. Additionally, in the gaseous phase, the molar ratio of $SO_2$ & $O_2$ is fixed ($SO_2 : O_2 = 2:1$).

Hence, the no. of components $\boxed{C = N - E = 4 - 2 = 2}$

* Systems formed by water & two salts without a common ion. For ex. $KNO_3$ & NaI in water. In this system, four different salts or their hydrates may occur in solid phases, namely $KNO_3$, NaI, KI & $NaNO_3$. To specify the composition of all possible phases, four components are necessary consisting of water & any three of the possible four salts. Hence, it is a four component system.

equ$^n$s involved in the system are

$KNO_3 \rightleftharpoons K^+ + NO_3^-$

$NaI \rightleftharpoons Na^+ + I^-$

$KI \rightleftharpoons K^+ + I^-$

$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$ and one equ$^n$ for electrical neutrality of the sol$^n$.

No. of constituents = 9 ($KNO_3$, NaI, $NaNO_3$, KI, $K^+$, $NO_3^-$, $I^-$, $Na^+$, $H_2O$)

No. of equations = 5

So $C = N - E = 9 - 5 = 4$

## Degree of freedom or Variance

The degree of freedom is the minimum no of independently intensive variables (such as temp, Pressure & concentration) that must be specified in order to describe the state of a system completely.

For ex. * The state of a certain amount of pure gas may be described completely by any two of three variables (T, P, & density). If any two are known, third can be calculated. So for this system $f = 2$ & it is a bivariant system.

* In the system water $\rightleftharpoons$ water vapor, only one intensive variable is required to describe the state. At any given temp, the VP in equ$^m$ with liquid water is fixed in value. Therefore, the system has $f = 1$, & is called as univariant system.

* For equ$^m$ ice $\rightleftharpoons$ water $\rightleftharpoons$ water vapor all are in equ$^m$, no conditions can be varied, as three phases can coexist only at a particular T & P. The system has therefore zero degree of freedom & it is called as invariant or non-variant.

## Advantages of phase rule

① It is applicable to both physical & chemical equ$^m$.

② It is applicable to macroscopic system & therefore, information about molecular structure is not required

③ It indicates that different system having same no. of degrees of freedom behave similarly

④ It predicts the behavior of a system under different sets of intensive variables (T, P, Conc)

⑤ It provides a convenient method for classification of equ$^m$ states of system with the help of phases, components & degree of freedom

⑥ It helps in deciding whether under a set of conditions: a) various substances would coexist (or)

b) some of the substances present would be interconverted (or)

c) some of the substances present would be eliminated.

## Limitations of phase rule

① It is applicable only for the systems in equilibrium. Therefore, it is of no use for the systems which attain the state of equ$^m$ very slowly.

② It is applicable to a single equ$^m$ state & does not indicate about the other equ$^m$ states in the system.

③ It considers only the intensive variables such as T, P & conc. It does not consider the other factors ~~such as~~ like influence of electric field, magnetic field.

④ It considers ~~the~~ only the no. of phases, but does not take into consideration of the relative amount of various phases.

⑤ It requires that solid & liquid phases are not present in such finely devided form, ~~otherwise~~ that deviation in VP (from natural values) take place.

⑥ It requires all the phases of a system to be present under same conditions of temp & pressure.

## Phase diagram

Phase diagram is a graphical representation formed by plotting the values of independent intensive variables like T, P & conc., to summarize the conditions under which the different states of a substance are stable. The phase diagram shows properties of the substance, such as MP, BP, phase-transition points & triple points. Every point on the phase diagram represents a state of the system since it describes the values of T & P.

## Phase diagram for One component system

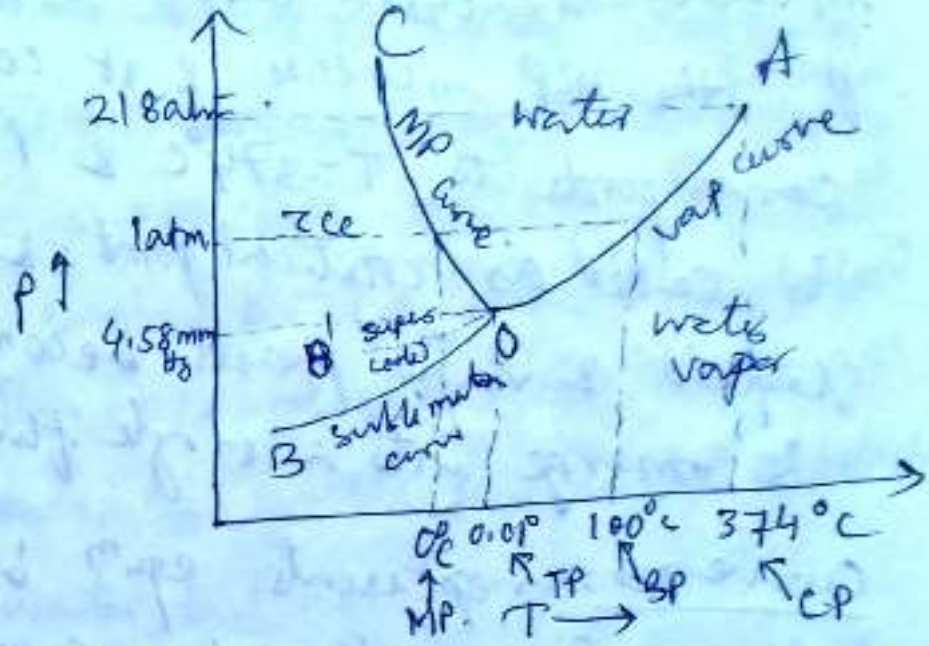
For one component system, the phase diagram is a two-dimensional plot, where P & T are chosen as two independent variables

Water system consists of only one component i.e. $H_2O$. Water exists in three different phases ice, water & water vapor. The maximum no. of degrees of freedom in this system is two when only one phase is stable at equilibrium.

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

The phase diagram for water is devided into three areas by the lines BO, OC & OA. Area BOC, COA & BOA respectively represent the conditions of T & P where only ice, water, water vapor

exist. In these regions, it is necessary to specify both T & P for defining the system completely. These areas has two degree of freedom & is called bivariant. $F = 1 - 1 + 2 = 2$.




Curve OC is called as MP, or FP or Fusion curve & represents the equ^m between ice & water. The -ve slope of the curve shows that MP of ice decreases with increase in P & ice melts with decrease of volume. Degree of freedom, $F = C - P + 2$
$= 1 - 2 + 2 = 1$.

So Curve OC is univariant
That means it is enough to specify either T or P in order to describe the system completely.
For ex. at 1 atm P, ice has only one MP i.e. 0°C.

Curve OA: is called vaporization or VP curve & represents the equ^m between water & vapor. It shows the VP of water at different T.

Curve OA has $F = 1 - 2 + 2 = 1$. Hence, to describe the system along line OA, it is enough to know either T or P. As the other variable is automatically fixed in value. The curve shows that with increase in P, the BP increase & it continues till point A corresponds to $T = 374°C$ & $P = 218$ atm. This point is called as critical point. & at this point, the liquid & vapor phases become indistinguishable & merge into a single fluid.

<u>Curve OB</u>: represents equ$^m$ bet$^n$ ice & vapor & called as sublimation curve. It shows the VP of ice at different Temperatures. Along line OB, No. of degrees of freedom is 1 (univariant system).

<u>Triple point O</u>: The point 'O' where the curve OA, OB, OC meet is known as Triple point. At this all the three phases of water are in coexist equ$^m$. The TP corresponds to $T = 0.01°C$ & $P = 4.58$ mm Hg.

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

Hence, the point 'O' is nonvariant or Invariant. Upon changing either T or P, the three phases would

no longer coexist.

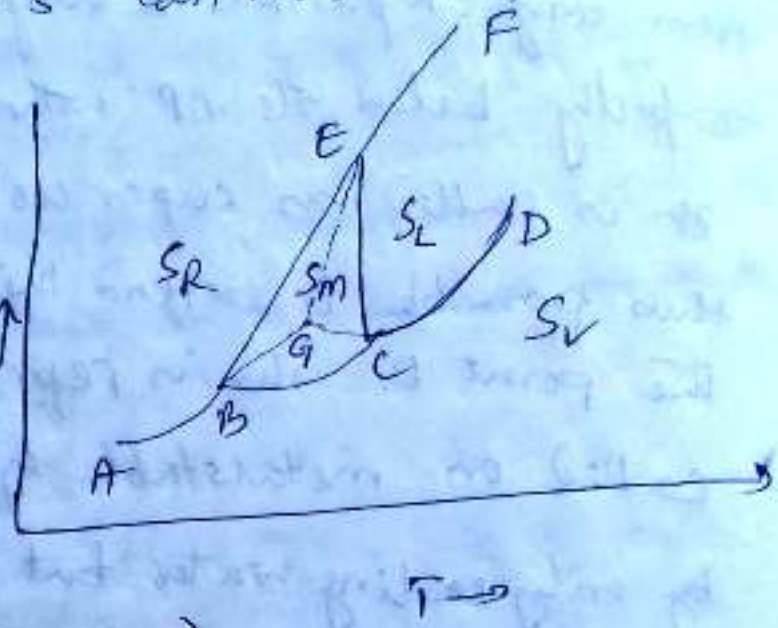
Curve OB': represents the metastable equ$^m$ bet$^n$ liquid water & its vapor. ~~when~~ pure water (free from any impurities & suspended particles) ~~is called~~ cooled rapidly below its MP without separation of solid, ~~it~~ is called as supercooled water and it is thus possible to extend the OB curve even below the point O. This is represented by curve OB'. called as metastable equ$^m$ & this can be approached by only cooling water but not by heating ice. The metastable VP of supercooled water is higher than the VP of ice. It is very unstable. A slight disturbance shifts the metastable equ$^m$ to stable equ$^m$ state.

## Sulfur system

Sulfur exists in four different phases: rhombic sulfur ($S_R$), Monoclinic sulfur ($S_m$), liquid sulfur ($S_L$) & Sulfur vapor ($S_V$). All these four phases can be represented by only one component i.e. S. Hence one component system.

For one component system, as the minimum value of F is zero, i.e. max. no. of phases that can coexist simultaneously is three. Therefore, all the four phases of S can not coexist.

G = 115°C, 0.03 mmHg.
B = 95.6°C 0.006 mmHg
C = 120°C, 0.04 mmHg
E = 151°C, 1288 mmHg




<u>Areas (Bivariant System)</u>

1. Area below ABCD: only $S_V$ exist.
2. Area right to DCEF: only $S_L$ exist.
3. Area left to ABEF: only $S_R$ exist.
4. Area BCE: only $S_M$ exist.

In all the above areas, only one phase exists & $F = 1 - 1 + 2 = 2$
Thus, in order to define the system completely, two variables, T & P are needed. Hence the areas represent a bivariant system.

Stable Curves (univariant system)

1. Curve AB: represent sublimation curve for $S_R$ & equ$^m$ ~~between~~ $S_R \rightleftharpoons S_V$. System has one degree of freedom, $f = 1-2+2 = 1$.

2. Curve BC: It is the sublimation curve for $S_M$ & represents $S_M \rightleftharpoons S_V$. This gives variation of VP of $S_M$ with T. The system is univariant.

3. Curve CD: is VP or vaporisation curve for $S_L$ & represents $S_L \rightleftharpoons S_V$. This curve starts at C, which is MP of $S_M$ & stops at D, which is the critical temp. Beyond D, there is only $S_V$ present.

4. Curve BE: It is transition curve & represents equ$^m$ between $S_R$ & $S_M$. The +ve slope indicates that transition temp increases with increase in P. It also indicates $S_R$ is heavier than $S_M$. The curve terminates at point E, beyond which $S_M$ disappears.

5. Curve CE: It is MP or fusion curve for $S_M$. & represent $S_M \rightleftharpoons S_L$. The +ve slope indicates that the MP of $S_M$ is raised by increase in P.

6. Curve EF: It is MP curve of $S_R$. It shows that MP of $S_R$ increases with increase in P. The equ$^m$ exist along EF curve is $S_R \rightleftharpoons S_L$.

metastable curves

(7) Curve BG: It is metastable sublimation curve of $S_R$. Along this curve metastable $S_R \rightleftharpoons$ metastable $S_V$ & the system is univariant. If the temp of stable $S_R$ is allowed to rise rapidly, the transition of $S_R$ into $S_M$ does not take place at B, rather the curve AB extends to G, which is the MP of ~~metal~~ metastable $S_R$.

(8) Curve CG: It is the continuation of DC and is called VP curve of supercooled $S_L$. If $S_L$ is allowed to cool very carefully & rapidly, the solid phase will not separate at C. Thus the curve DC can be extended to G by supercooling $S_L$. CG represents metastable equ$^m$ between supercooled $S_L$ & $S_V$

(9) Curve EG: is metastable fusion curve of $S_R$ or MP curve of metable $S_R$. Along this curve $S_R$ is in metastable equ$^m$ with $S_L$. This curve express the effect of pressure on metastable $S_R$.

Triple points $\Rightarrow$ P=3, C=1 so F = 1 − 3 + 2 = 0 (Invariant)

1) Point B represents $S_R \rightleftharpoons S_M \rightleftharpoons S_V$ corresponds to T = 95.6°c & Press 0.006 mm Hg

(ii) Point C represents $S_M \rightleftharpoons S_L \rightleftharpoons S_V$. It corresponds to $T = 120°c$ & $P = 0.04$ mm Hg

(iii) Point E: represents equ$^n$ $S_M \rightleftharpoons S_L \rightleftharpoons S_R$ & corresponds to $T = 151°c$ & $P = 1288$ mm Hg.

(iv) Metastable triple point G ~~rep~~ represents the equ$^m$ betn metastable $S_R \rightleftharpoons S_L \rightleftharpoons S_V$.

The point corresponds to $T = 115°c$, $P = 0.03$ mm Hg

## Two component System

The phase diagram of a two-component system is a 3-D plot., where in addition to P & T, mole fraction must be included. However, in practice, this 3-D plot is converted to a 2D plot by keeping any of the three variables constant. Usually the pressure constant (usually equal to atm. pressure). Such phase diagram are called isobars.

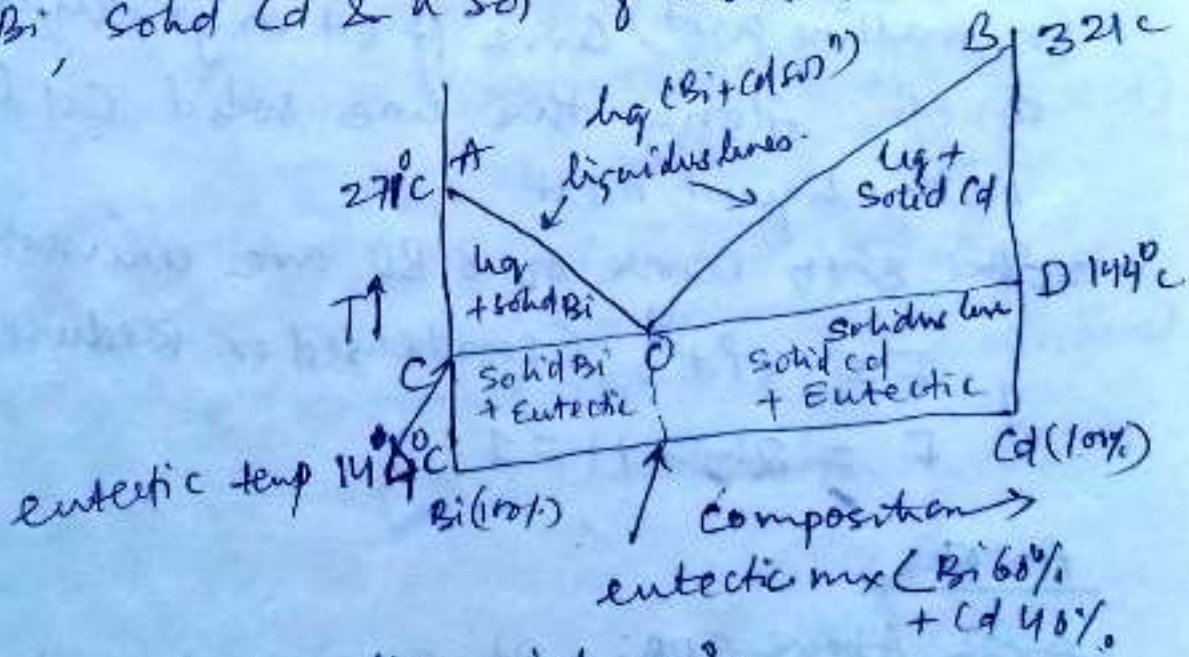
## Bi-Cd System (two component System)

Bi-Cd System is a simple two component eutectic system. A binary system, consisting of two substances which are miscible in all proportion in their molten (liquid) phase but do not react ~~with~~ chemically is known as eutectic system.

In Bi-Cd system, only solid & liquid phases are present & the vapor phase is not considered. Thus the pressure has negligible or no effect on the equ$^m$ & hence to

called as condensed phase system. The phase rule to be applicable here is reduced or condensed phase rule which can be represented as $F' = C - P + 1$ (1 refers to T. since only the variable temp is ~~air~~ considered)

The mutual solubility of Cd & Bi in solid state is extremely small but in the molten state, they are miscible in all proportions to form a homogeneous mixture. The system can have a maximum of 3 phases, namely solid Bi, solid Cd & a soln of molten Bi & Cd.




Pure Bi has a melting point 271°c and addition of Cd to ~~liq~~ Bi progressively decreases FP to a lowest T of 144°c at 40% Cd conc. Similarly pure Cd has MP 321°c & addition of Bi to liq Cd progressively decreases FP to a lowest T of 144°c at 60% Bi. ~~This point of T~~

This temp is called as eutectic Temp. Below this temp liquid phase can not exist. The phase diagram consists ~~the~~ of two lines AO & BO ~~are~~ (called as liquidus), four areas AOB, AOC, BOD. & area below COD line (called as solidus). and one point O' called as eutectic point.

<u>Curve AO</u>: It is the freezing point curve of Bi on gradual addition of Cd. Along this curve solid Bi is in equ$^m$ with liquid melt (sol$^n$).

<u>Curve BO</u>: It represents the freezing point (or melting point) curve of Cd on gradual addition of Bi. Along this line solid Cd is in equ$^m$ with liquid melt.

~~Both the~~ Both Curve AO & BO are univariants.

$F = C - P + 1$ (condensed or Reduced phase rule)

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

<u>Areas</u>:

<u>Area Above AOB</u>: It consists of only one phase i.e., liquid sol$^n$. The degree of freedom is found to be 2. $F = 2 - 1 + 1 = 2$.

Hence the system is bivariant & both temp and composition are required to be mentioned to define the system completely

Area AOCA: It involves two phases, i.e. solid Bi & liquid solⁿ containing Bi & Cd.

Area BODB: It contains also two phases i.e. solid Cd & liquid solⁿ containing Bi & Cd.

so both these areas are univariant.

$F = 2 - 2 + 1 = 1$. $C = 2$ (Cd & Bi)
$P = 2$ (Solid + liquid solⁿ)

(*) Area below COD: It represents a solid mixture of Bi & Cd and eutectic. The line is called as solidus as everything is in solid form below this line with temp 144°C. The number of phases are two (either Bi + eutectic or solid Cd + eutectic) & no. of components 2 (Bi & Cd).

So $F = 2 - 2 + 1 = 1$ (univariant)

Here only composition is required to be mentioned to explain the system completely.

→ (*) In these areas, (AOCA & BODB), for any given temp, the composition of the liquid phase can be ~~obtained~~ determined from the respective liquidus lines after solidification of pure Bi & pure Cd.

Eutectic point 'O': The intersection point of two curves AO & BO is known as eutectic point & at this point three phases, solid Bi, solid Cd & the liquid melt are in equ$^m$. On applying phase rule, we get

$F = 2 - 3 + 1 = 0$ (Thus point 'O' is invariant)

Both temp & composition are fixed, that is $T = 144°C$ & composition is (60% Bi & 40% Cd). If temp is increased above 'O', the solid phase will disappear & if temp decreases, below 'O', the liquid phases disappear.

Eutectic mixture: It is a solid sol$^n$ of two or more substances having the lowest freezing point of all possible mixture of the components.

## 4.8 Lead–Silver System

Lead–silver system is an example of a simple eutectic system. Silver and lead are miscible in all proportions and do not react chemically. When molten silver and lead are mixed together in all proportions, a single homogenous solution is formed. The system consists of four phases:

(i) Solid silver

(ii) Solid lead

(iii) Solution of molten silver and lead

(iv) Vapour

Since pressure has no effect on the equilibrium, the system can be represented by a temperature - concentration diagram at constant atmospheric pressure. As the gaseous phase is practically absent, one variable is neglected and the condensed phase rule

F = C – P + 1 will be applicable.

The phase diagram of lead–silver system is shown in Fig. 4.5.
It consists of the following:

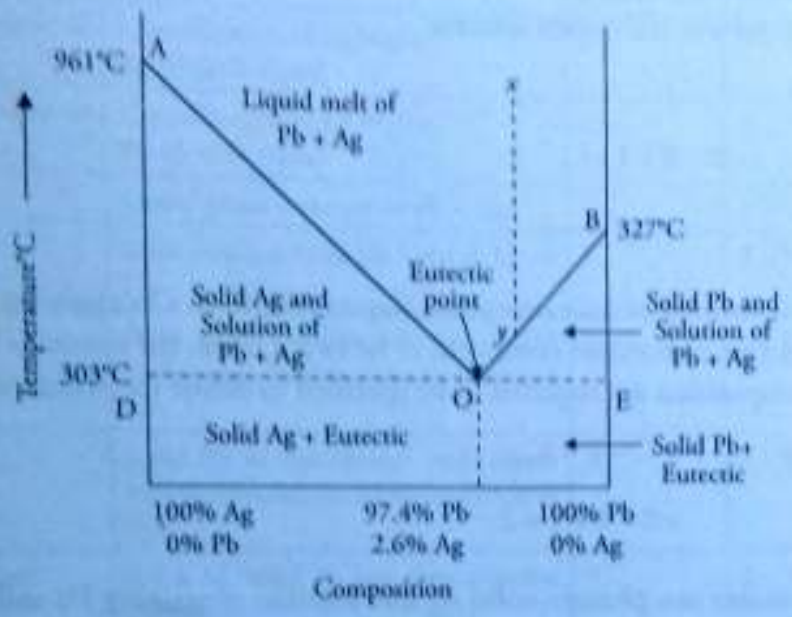



**Figure 4.5** *Phase diagram of lead–silver system (not to scale)*

**(a) Points**

Point A → Freezing point of pure Ag (961°C)

Point B → Freezing point of pure Pb (327°C)

Point O → Eutectic point (303°C)

**(b) Curves**

Curve AO → Freezing point curve of Ag on gradual addition of Pb

Curve BO → Freezing point curve of Pb on gradual addition of Ag

**(c) Areas**

Area above AOB

Area ADOA

Area BOEB

Area below DOE

**Points** In the phase diagram, point A represents the melting point of pure Ag and point B represents the melting point of pure Pb. At these points, C = 1, P = 2 (pure Ag in equilibrium with its liquid or pure Pb in equilibrium with its liquid), hence F = C – P + 1; 1 – 2 + 1 = 0.

**Curves** It is clear from the diagram that addition of Pb to pure Ag lowers the melting point of Ag; similarly, addition of Ag to pure Pb lowers the melting point of Pb.

The curve AO represents the melting point of Ag on gradual addition of Pb. Along this curve, solid Ag and solution are in equilibrium.

The curve BO represents the melting point of Pb on gradual addition of Ag. The curve indicates that the melting point of Pb gradually falls on addition of Ag. Along this curve, solid Pb and solution are in equilibrium.

Both AO and BO represent univariant systems

$C = 2 \quad P = 2$

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

**Areas**

*Area above AOB* It consists of only one phase (liquid solution). On applying the reduced phase rule equation, the degree of freedom comes out to be two. Hence, the system is bivariant and both temperature and composition are required to be specified to define the system completely

$C = 2, \quad P = 1 \qquad F = C - P + 1$

$= 2 - 1 + 1 = 2$

*Area ADOA* It contains two phases—solid Ag and solution containing Pb and Ag

*Area BOEB* It represents the phases—solid Pb + solution containing Pb and Ag. Both these areas have two phases and are univariant.

$F = C - P + 1 \qquad C = 2$ (Pb and Ag)

$= 2 - 2 + 1 = 1 \quad P = 2$ (Liquid + solid phase)

*Area below DOE* It represents a solid mixture of Pb or Ag with eutectic. The number of phases is 2 (either Ag or Pb + eutectic) and the system is univariant.

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

$= 2 - 2 + 1 = 1$

**Eutectic point O**

The two curves AO and BO intersect at point O at a temperature of 303°C. The point O is known as the eutectic point. At this point, three phases—solid Ag, solid Pb and the melt are in equilibrium. On applying the phase rule equation, we get

$F = C - P + 1$

$= 2 - 3 + 1 = 0$

Thus, the system at this point is invariant. Both temperature (303°C) and composition (Ag 2.6% and Pb 97.4%) are fixed at this point. If the temperature is increased above the eutectic point, the solid phase (silver or lead) will disappear and if the temperature decreases below the eutectic point, the solution phase disappears and only the solid phase (eutectic + solid lead or silver) will remain.

The various areas, curves, and points on the Pb–Ag phase diagram are tabulated in Table 4.3.

**Table 4.3** Phase diagram of lead -silver system

| Region of the phase diagram | Phases in equilibrium | Number of phases (P) | Degree of freedom (F) (C-P+1) |
|---|---|---|---|
| AO(Freezing point curve of Ag on addition of Pb) | Crystallization of Ag begins Ag (s) $\rightleftharpoons$ liquid | 2 | 2 – 2 + 1 = 1(univariant) |
| BO(Freezing point curve of Pb on addition of Ag) | Crystallization of Pb begins Pb (s) $\rightleftharpoons$ liquid | 2 | 2 – 2 + 1 = 1(univariant) |
| Area above AOB | Liquid phase (solution of Pb + Ag) | 1 | 2 – 1 + 1 = 2(bivariant) |
| Area below DOE | Solid mixture (eutectic + solid Ag or Pb) | 2 | 2 – 2 + 1 = 1 (univariant) |
| Area ADOA | Solid Ag in equilibrium with liquid having composition given by the curve OA | 2 | 2 – 2 + 1 = 1 (univariant) |
| Area BOEB | Solid Pb in equilibrium with liquid having composition given by the curve OB | 2 | 2 – 2 + 1 = 1 (univariant) |
| Point O (eutectic point) | Solid Ag, solid Pb and their solution coexist | 3 | 2 – 3 + 1 = 0 (invariant) |

## Application of Ag–Pb system

**Pattinson's process for desilverization of argentiferous lead** The process of heating argentiferous lead containing a very small quantity of Ag (0.1% by mass) and cooling it to get pure lead and liquid rich in silver is called Pattinson's process.

Argentiferous lead is first heated to a temperature above its melting point. The system consists of only the liquid phase represented by point *x* in Fig. 4.5. It is then allowed to cool. The temperature of the melt will fall along the perpendicular line *xy* without change in composition. As the point *y* is reached, lead will begin to crystallize and the percentage of silver will increase in the solution. The system moves along the curve *yo*. The melt continues to be richer and richer in silver until the point O is reached. At point O, the percentage of silver is 2.6% by mass.

After removing the lead that separates out, the liquid is cooled further to give a mixture of eutectic composition (97.4% Pb + 2.6% Ag). Pure silver is obtained from this alloy by other processes like cupellation.

## Difference between melting point, triple point and eutectic point

- At melting point, a solid is in equilibrium with a liquid of the same composition.
- At triple point, three phases are in equilibrium.
- At eutectic point, two solids and a liquid are in equilibrium.

By definition, all eutectic points are melting points but the reverse is not true. Similarly, all eutectic points are triple point and not vice versa.