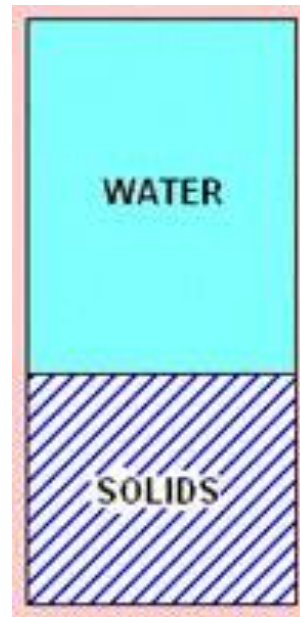


PHASE

- Phase is a *homogeneous*, *physically distinct*, and *mechanically separable portion* of matter present in a nonhomogeneous physico-chemical system.
- A phase is separated from other parts of the system by a definite boundary.



Three Phases
Heterogeneous System



Two Phases
Heterogeneous System



One Phase
Homogenous System



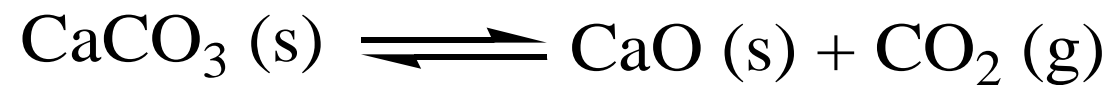
A system in which ice (solid), liquid water (liquid) and water vapour (gas) exists together. Each form of water is a separate phase.



Mixture of Oil and water
Heterogeneous system
with two distinct phases.



Mixture of Ethanol and water
– Homogeneous system
with only one phase



The system consists of two solid phases and one gas phase.

EQUILIBRIUM BETWEEN PHASES

- Phase equilibrium is the study of the equilibrium which exists between or within different states of matter namely solid, liquid and gas.
- The thermodynamic criterion for phase equilibrium is based upon the chemical potentials of the components in a system.
- Equilibrium is defined as a stage when chemical potential of any component present in the system stays steady with time.

Consider a system with only one component and exists in two phases say, α and β .

$$\mu_{\alpha} = \mu_{\beta}$$

Phase Equilibrium – Thermal, mechanical and chemical equilibrium

GIBBS PHASE RULE

- Phase rule is a generalization describing the equilibrium between different phases of a heterogeneous system.
- It qualitatively predicts the influence of changes in temperature, pressure and concentration on the equilibrium of a heterogeneous system.
- Phase rule relating the variables of a heterogeneous system in equilibrium was deduced by J. W. Gibbs in 1875 and hence it is also referred to as Gibbs phase rule.

Phase rule:

For a heterogeneous system in equilibrium, the number of degrees of freedom (F) is given by:

$$\mathbf{F = C - P + 2}$$

C – No. of components present in the equilibrium system

P - No. of phases present at the equilibrium.

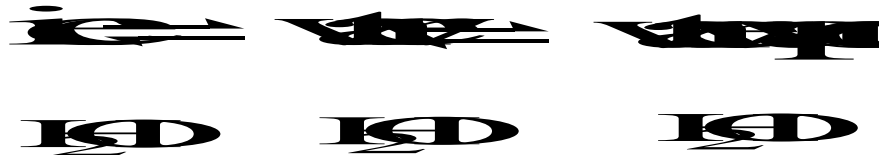
Phase (P)

Phase is a homogeneous, physically distinct, and mechanically separable portion of matter present in a heterogeneous system.

Number of Components (C)

Number of Components (C) of a system in equilibrium is defined as the *minimum number of independent chemical constituents* by means of which the composition of each phase can be expressed either directly or in terms of chemical equation.

Water system



one component system

Mixture of Oil and water

Two phases are expressed by two chemical constituents for oil and water respectively. Hence no. of components in this equilibrium is 2.



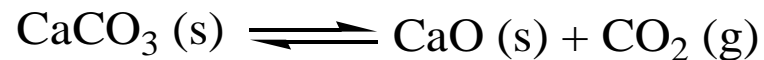
Mixture of Ethanol and water – Single phase.

But 2 chemical constituents (C_2H_5OH and H_2O) are required to express the concentration.

Hence no. of components is **2**.



An equilibrium of $CaCO_3$ decomposition:



The composition of each phase can be expressed as follows:



Hence no. of components is **2**.

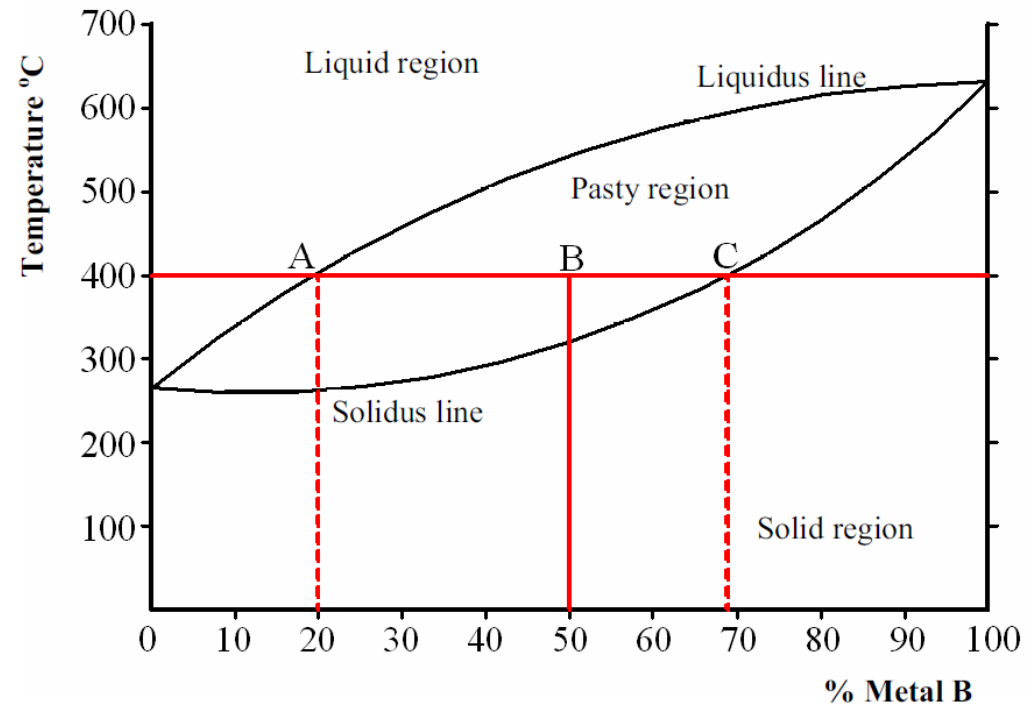
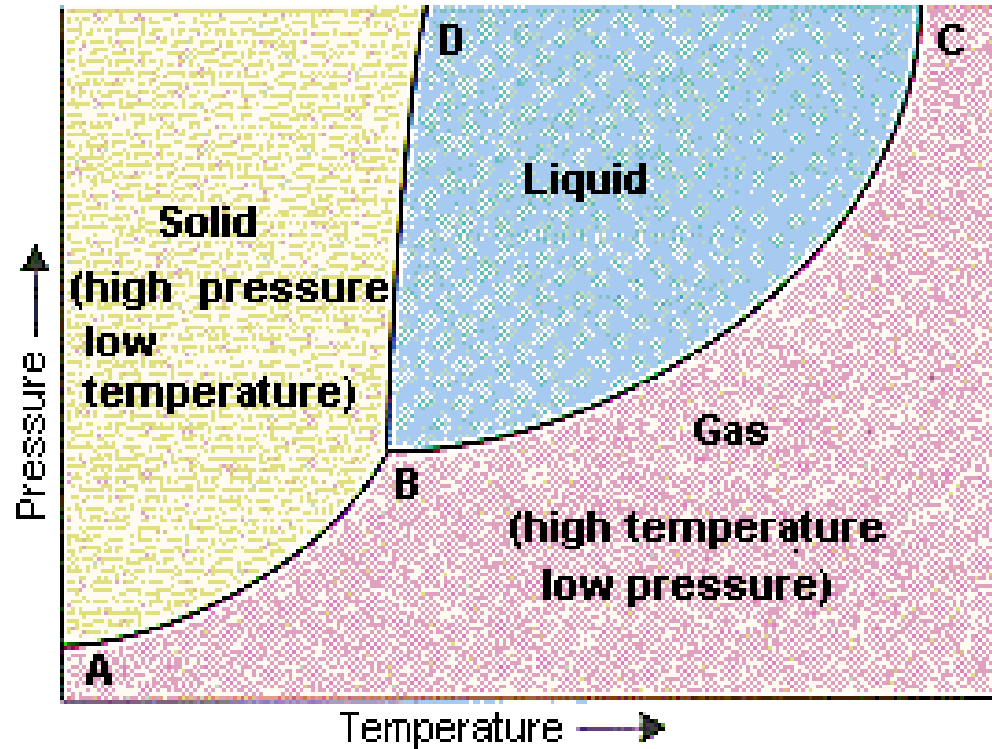
Degrees of Freedom (F)

The degrees of freedom (F) of a system may be defined as the minimum number of independent variables such as temperature, pressure and concentration, which must be specified in order to define the state of the system at equilibrium completely.

PHASE DIAGRAM

- Phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure.
- A typical phase diagram has pressure on the y-axis and temperature on the x-axis.
- As we cross the lines or curves on the phase diagram, a phase change occurs.
- In addition, two states of the substance coexist in equilibrium on the lines or curves.

- Single phase regions are separated by lines where phase transitions occur, which are called phase boundaries.



ONE COMPONENT SYSTEM

A one-component system is a system involving one pure chemical. By applying Gibbs Phase rule, we get

$$F=C-P+2$$

$$F=1-P+2$$

$$F=3-P$$

When, $P=1$, $F=2$, i.e. the system is bivariant

When, $P=2$, $F=1$ i.e. the system is monovariant

When, $P=3$, $F=0$ i.e. the system is invariant

PHASE DIAGRAM OF WATER SYSTEM

- One Component System – H₂O
- Three phases – Solid, liquid and Gas

$$F=C-P+2$$

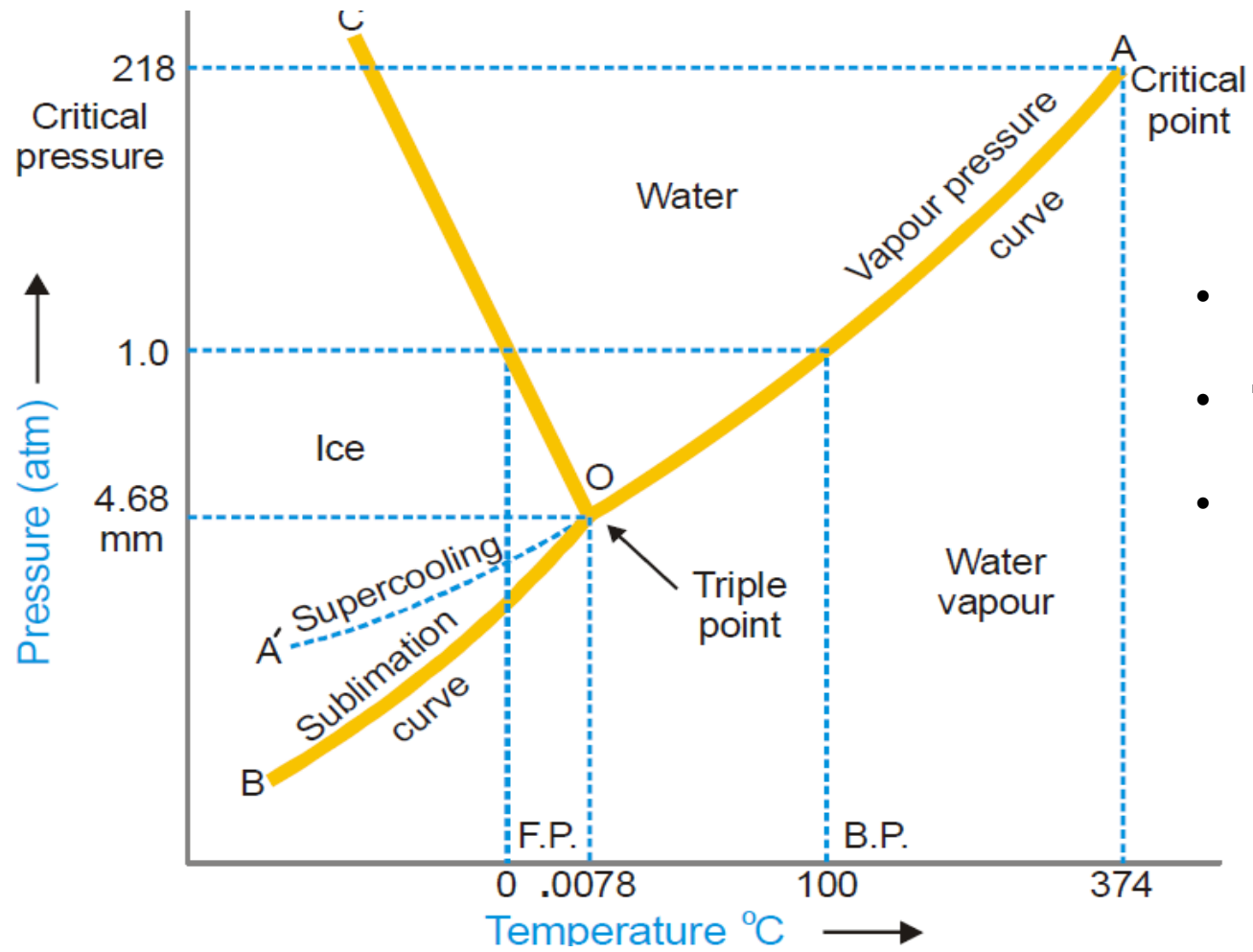
$$F=1-P+2$$

$$F=3-P$$

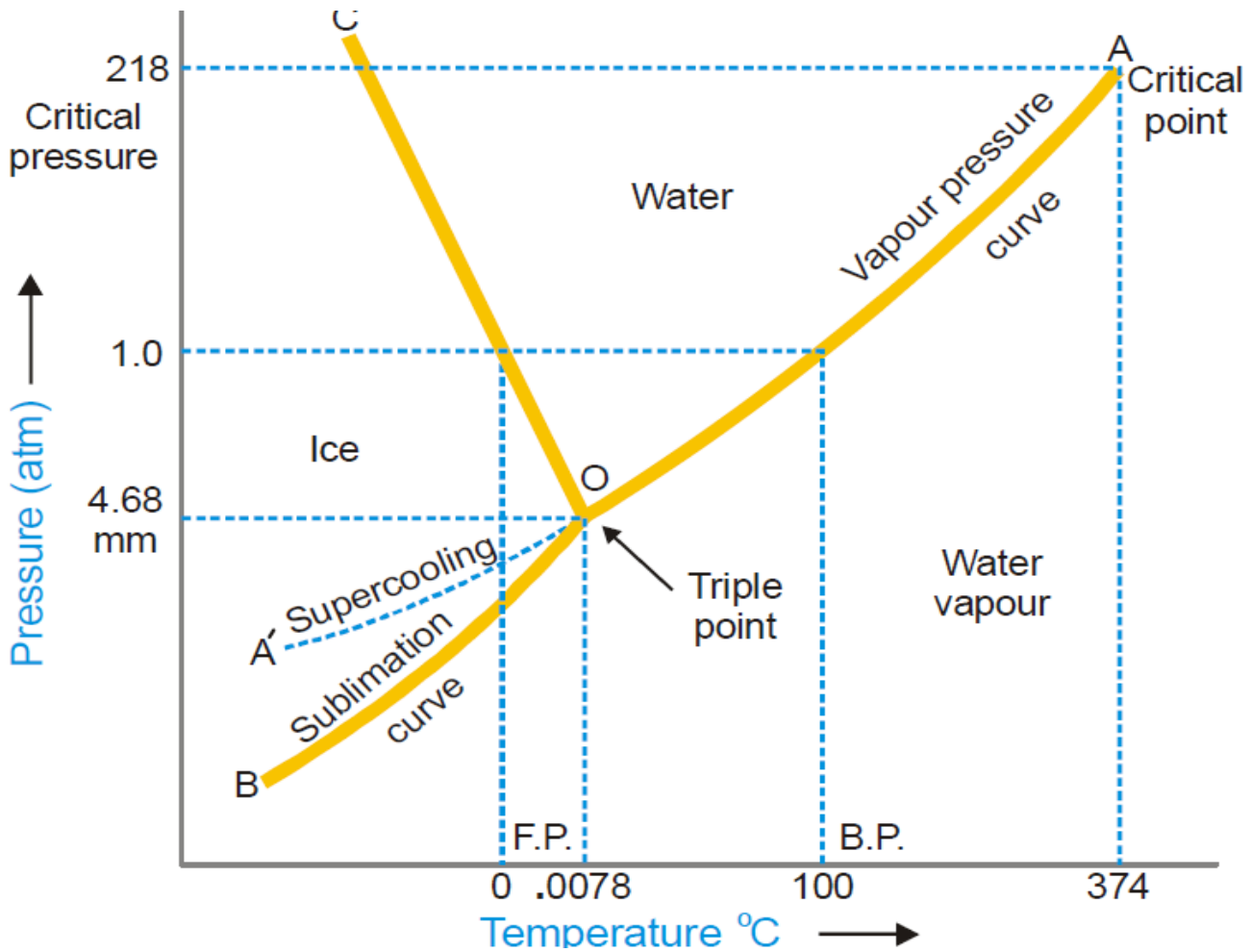
When, $P=1$, $F=2$, i.e. the system is bivariant

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When, $P=3$, $F=0$ i.e. the system is invariant



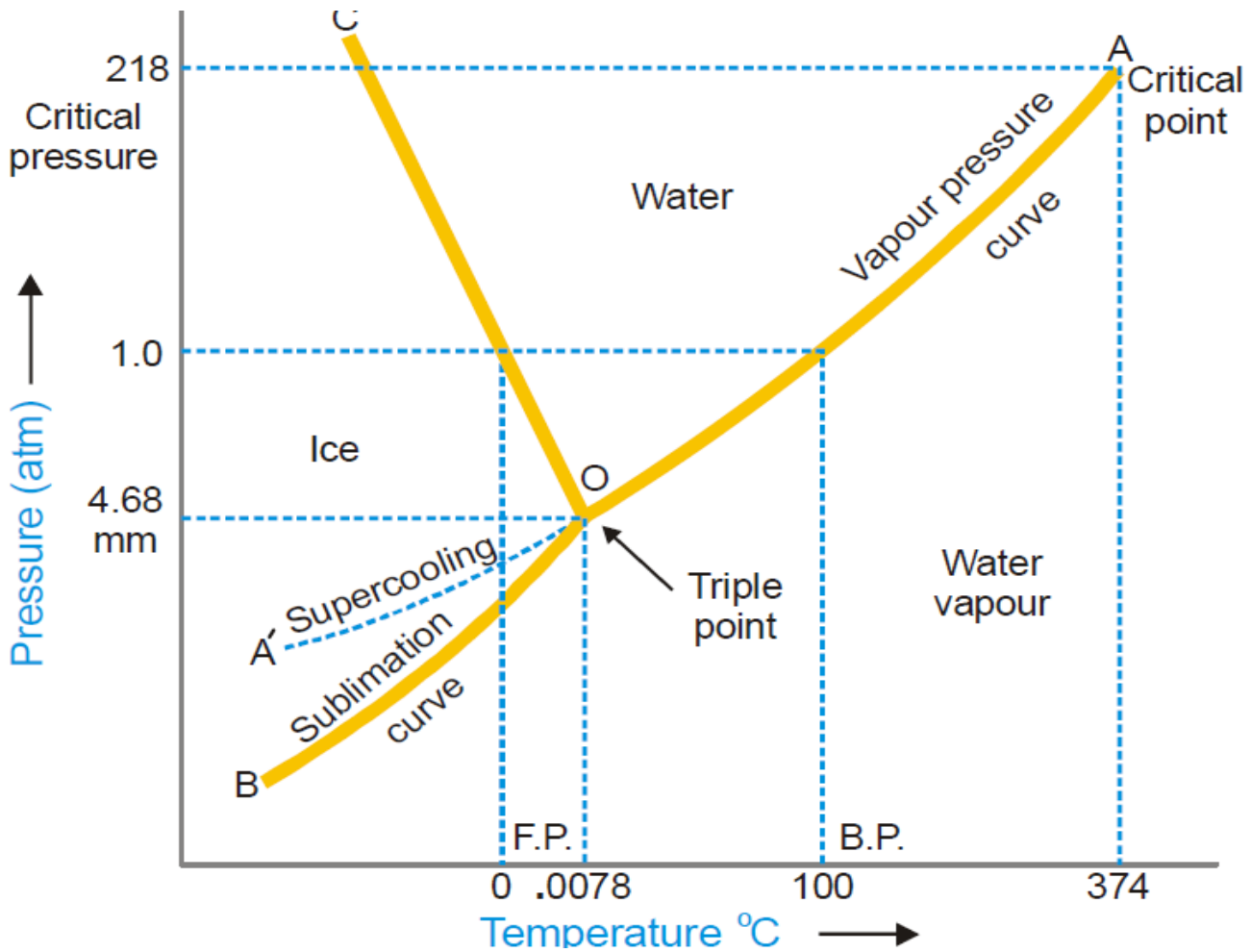
- Four Curves – OA, OB, OC, OA'
- Three phases – ice, liquid and vapour
- One point - O



Curve – OA

- Equilibrium between water & water vapour.
- Vapour pressure curve of water
- Applying phase rule

$$F=1-2+2 = 1$$
- System is univariant along the curve.
- Vapour pressure increases with temperature.

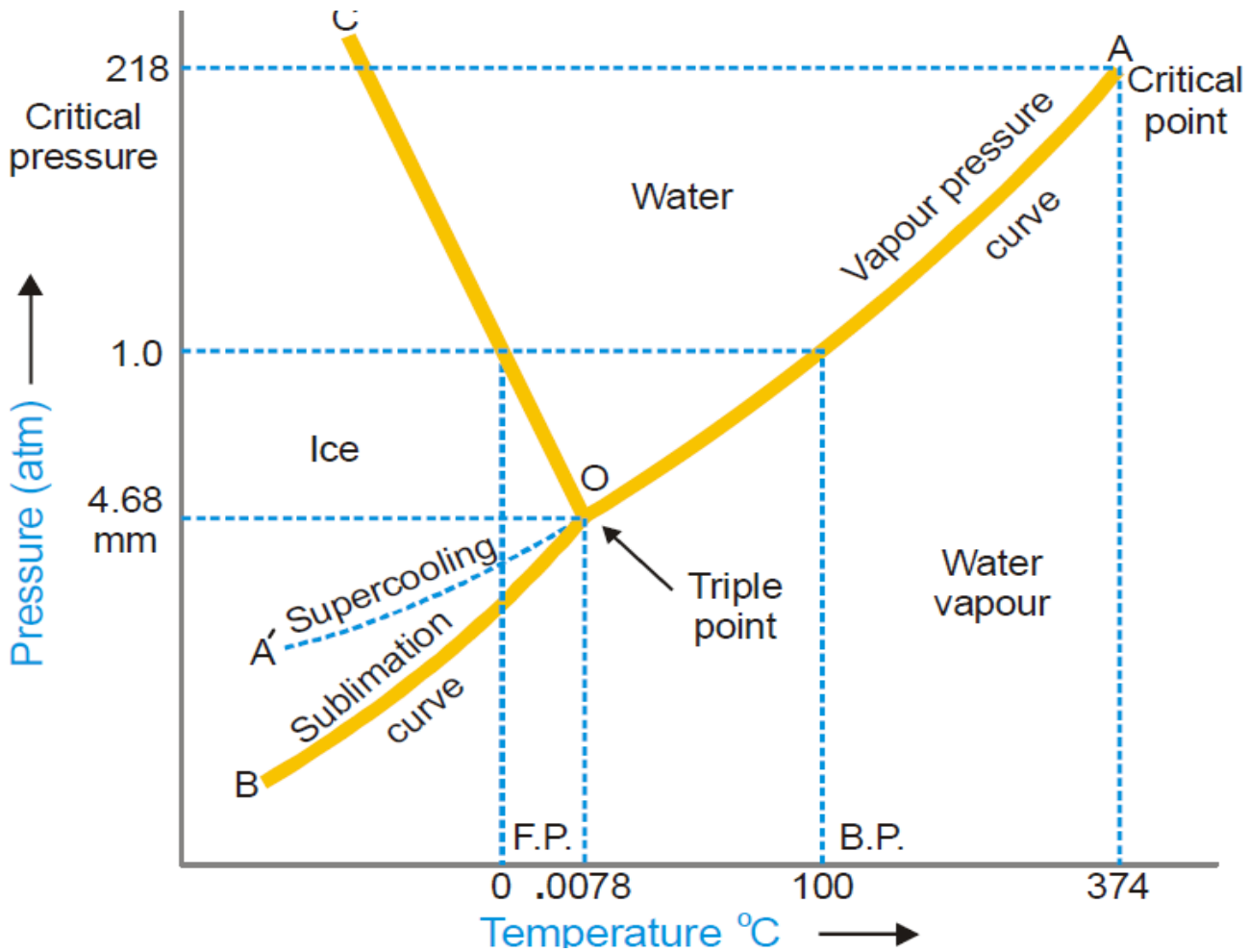


Curve – OB

- Equilibrium between ice & water vapour.
- Vapour pressure curve of ice or sublimation curve of ice.
- Applying phase rule

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

- System is univariant along the curve.
- Vapour pressure increases with temperature.

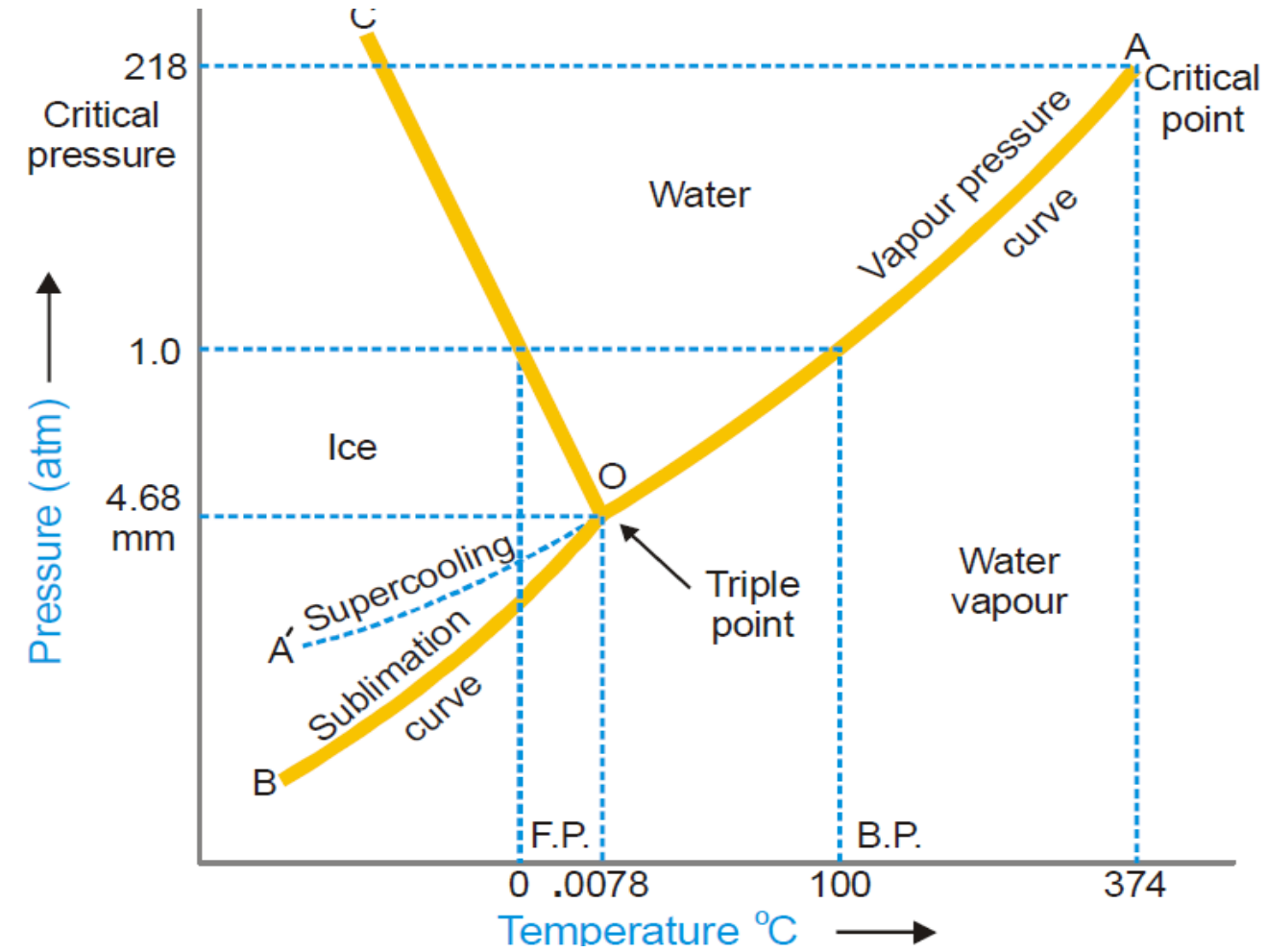


Curve – OC

- Equilibrium between ice & liquid water.
- Fusion curve of ice.
- Applying phase rule

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

- System is univariant along the curve.
- Melting point of ice or freezing point of water is lowered by increasing the pressure.

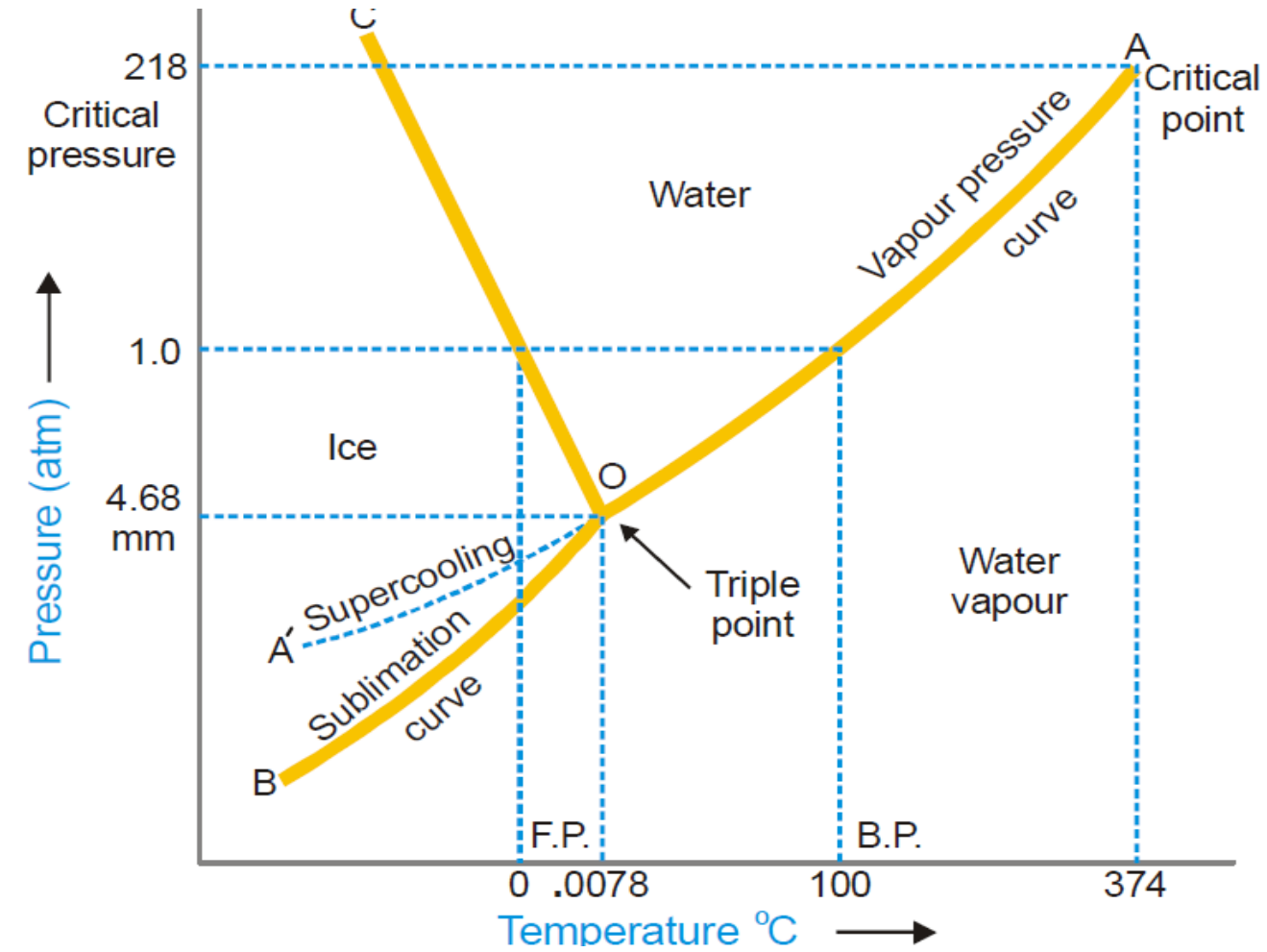


Curve – OA'

- Metastable equilibrium curve.
- Equilibrium between ice & water vapour.
- Due to supercooling.
- Applying phase rule

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

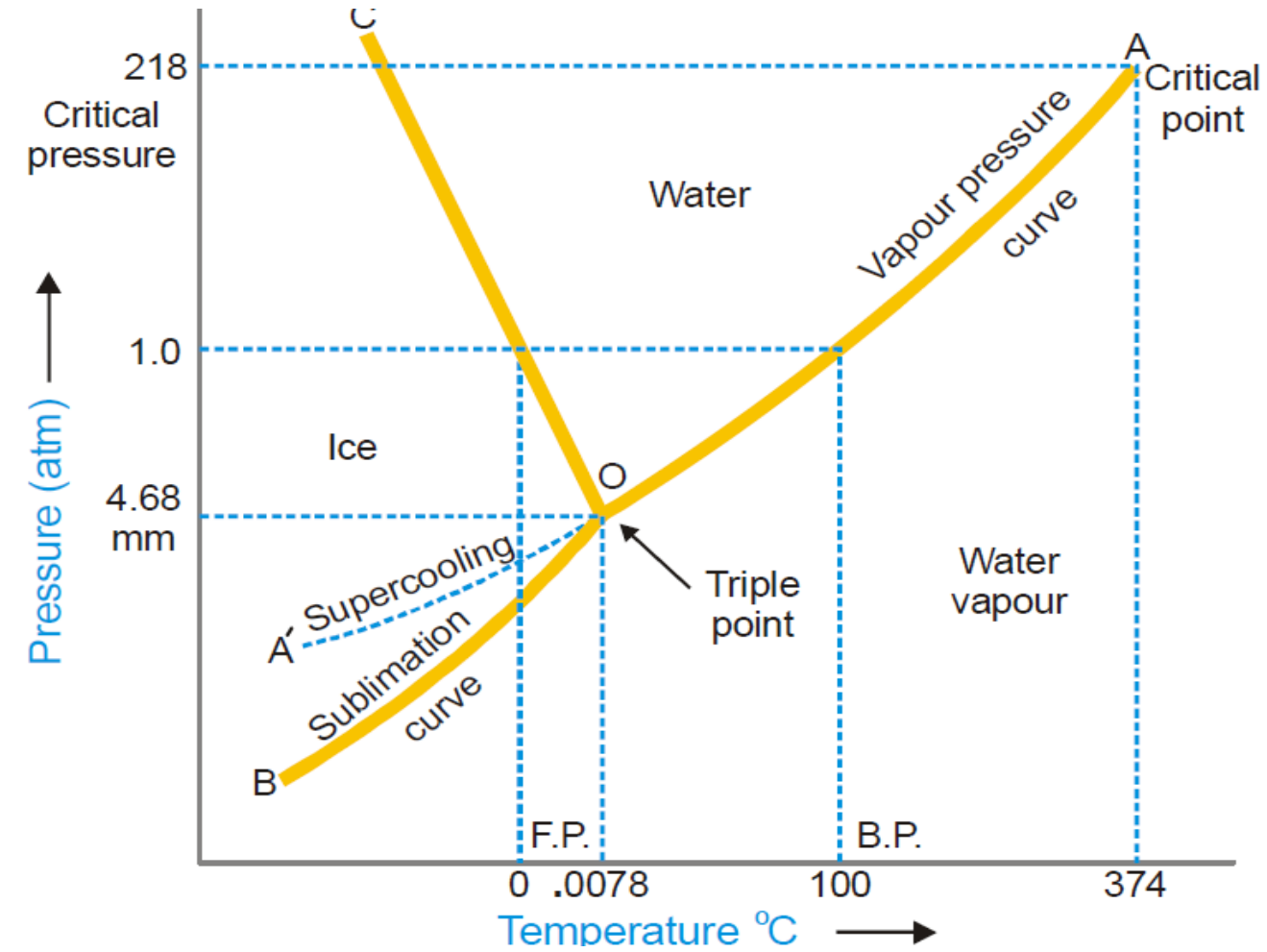
- System is univariant along the curve.
- Possible only from one direction.



POINT - O

- Three phases co-exist in equilibrium.
- 4.58 mm of Hg & 273.16 K
- Triple point of water.
- Applying phase rule

$$F=1-3+2 = 0$$
- System is inivariant along the curve.



AREA UNDER AOC - WATER

AREA UNDER AOB – WATER VAPOUR

AREA UNDER BOC – ICE

- Water – Single Phase
- Applying phase rule

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

- System is bivariant in within the area.

SULPHUR SYSTEM

The sulphur system is a one component system, since the only chemical individual representing the various phases is sulphur (S) itself. Different phases of sulphur are:

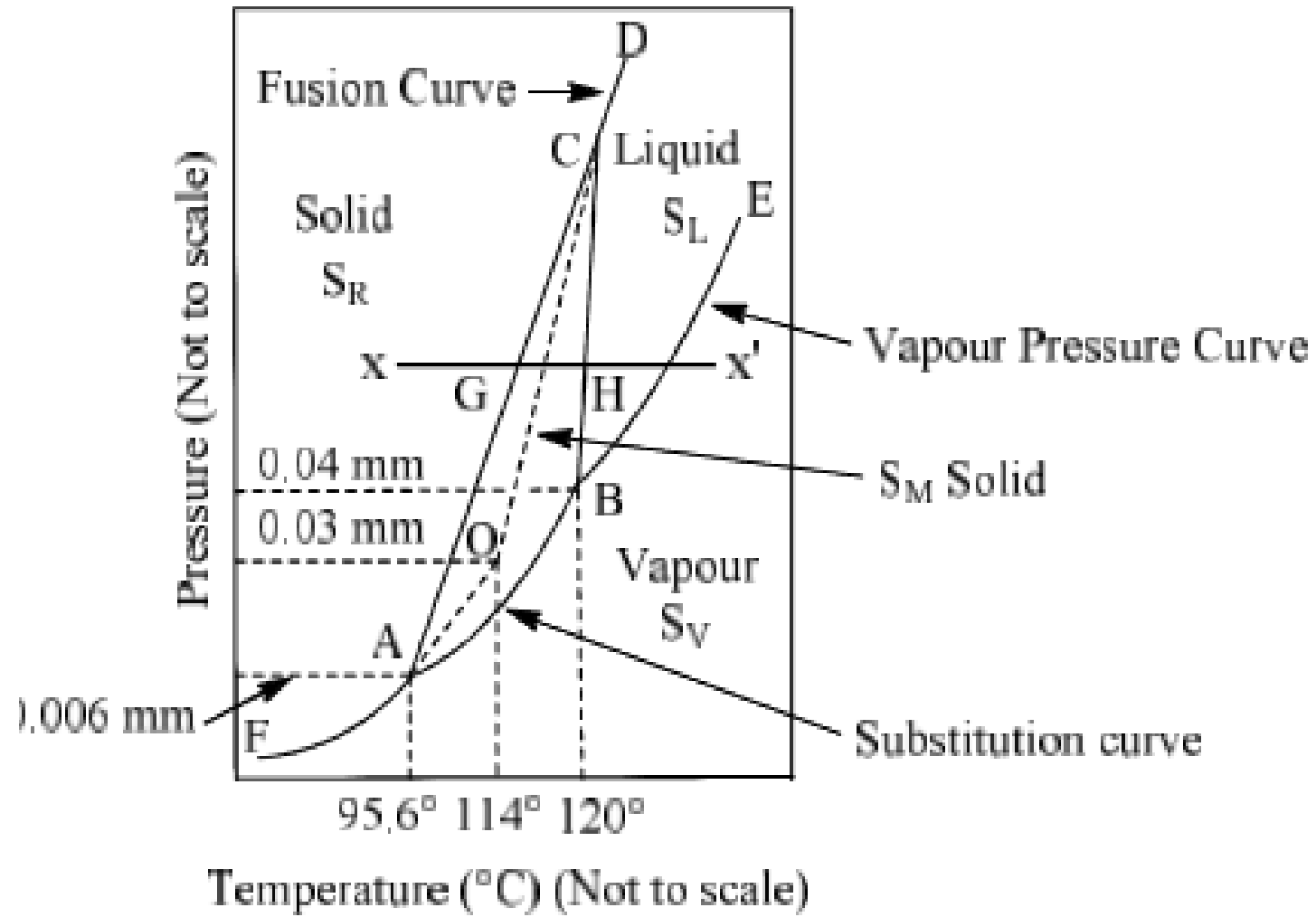
- Rhombic sulphur (S_R)
- Monoclinic sulphur (S_M)
- Liquid sulphur (S_L)
- Vapour sulphur (S_V)

The lowest possible degree of freedom possible in any one component system is zero.

Applying Gibbs phase rule:

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

- The maximum number of phases that can co-exist in equilibrium is 3.
- All the four phases cannot co-exist together.



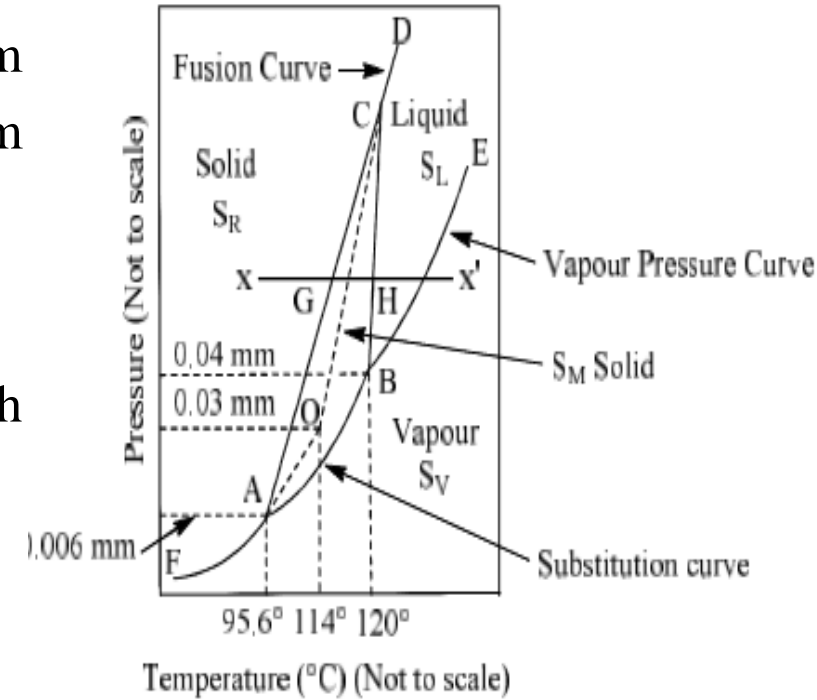
AREAS:

Curves FA, AB, BE, AC, BE and CD, where two phases are in equilibrium at different temperatures and pressures. These curves divide the diagram into four areas where only one phase exists.

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

Hence each area represent a bivariant system. It is necessary to specify both temperature and pressure.

- Area left to FACD : This area has only rhombic sulphur.
- Area below FABE: This area has only vapour sulphur.
- Area right to EBCD : This region has only liquid sulphur.
- Area surrounded by curves AB, BC and AC: This area has only monoclinic sulphur.



CURVES:

The curves in the phase diagram represents the conditions of temperature and pressure under which two phases coexist in equilibrium.

Applying phase rule:

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

Hence each area represent a monovariant system. In order to define the system at any point on the curve, either the temperature or pressure alone need be stated.

Curve FA : This curve is the sublimation or vapour pressure curve of rhombic sulphur (S_R).



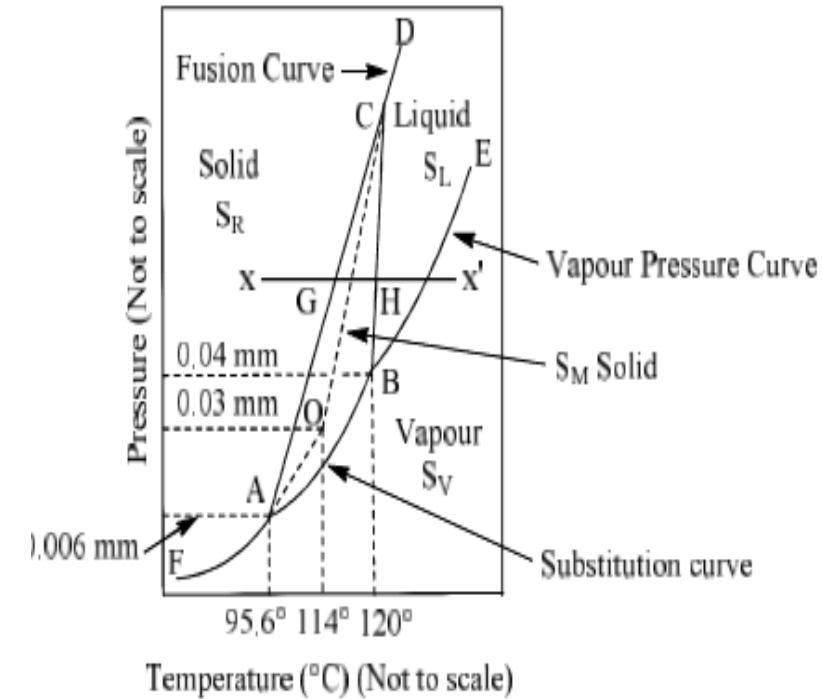
Curve AB : It is vapour pressure or sublimation curve of monoclinic sulphur (S_M).



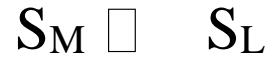
Curve BE : It is the vapour pressure curve of liquid sulphur (S_L).



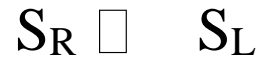
Curve AC : This is known as the Transition curve of S_R to S_M .



Curve BC : It is melting or fusion curve for monoclinic sulphur.



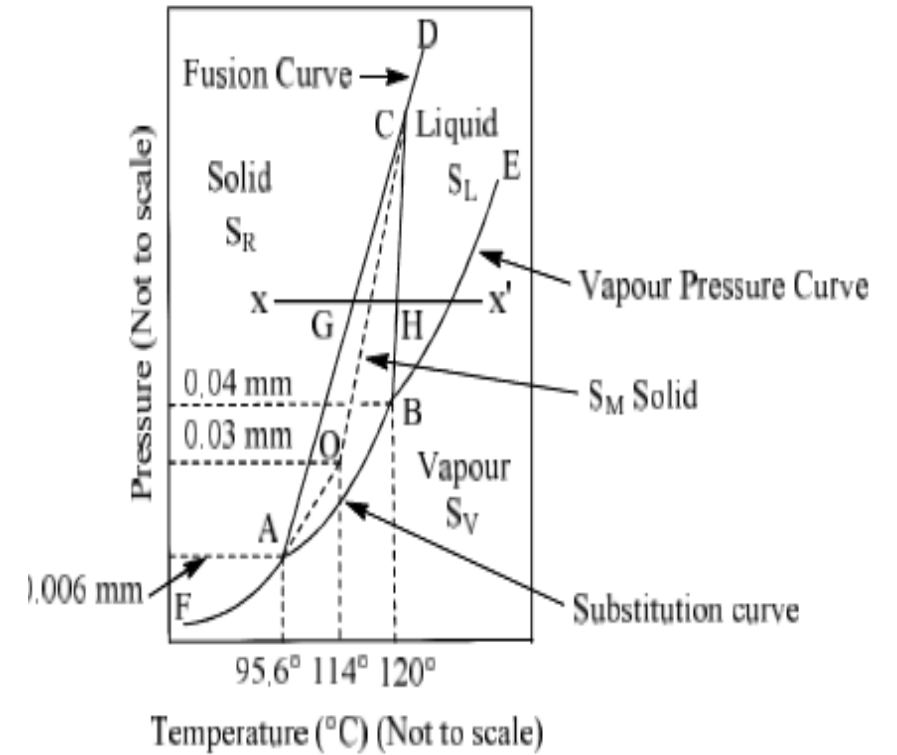
Curve CD : It is the fusion curve for rhombic sulphur.



Curve AO : Metastable equilibrium $S_R \rightleftharpoons S_V$

Curve OB : Metastable equilibrium $S_L \rightleftharpoons S_V$

Curve OC : Metastable equilibrium $S_R \rightleftharpoons S_L$



TRIPLE POINTS

There are four triple points in the sulphur system including the metastable triple point. The system is invariant at the triple point.

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

Triple Point at A :

$S_R \square \quad S_M \square \quad S_V$ 95.6 °C & 0.006 mm of Hg

Triple Point at B :

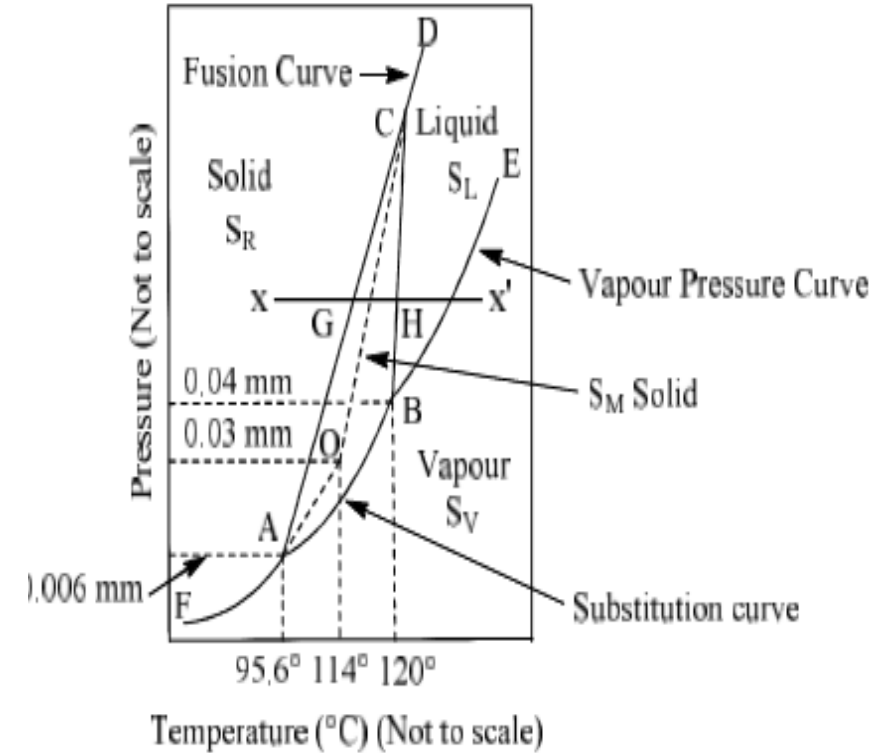
$S_M \square \quad S_L \square \quad S_V$ 120 °C & 0.04 mm of Hg

Triple Point at C :

$S_M \square \quad S_L \square \quad S_R$ 151 °C & 1290 atm

Metastable Triple Point at O :

$S_R \square \quad S_L \square \quad S_V$ 114 °C & 0.03 mm of Hg



PHASE EQUILIBRIA FOR TWO-COMPONENT SYSTEMS

The Gibbs phase rule for a two component system is given by:

$$F = C - P + 2$$

$$F = 2 - P + 2 \quad \text{or,} \quad F = 4 - P$$

Putting the lowest possible value for phases, 1, we get $F = 4 - 1 = 3$

- This requires a three dimensional space model for phase diagram which is difficult to construct on a paper.
- Pressure is kept constant in the study of two component systems involving solid-liquid equilibria.
- In solid-liquid equilibria, phases have little effect on small changes of pressure.

Since one degree of freedom is kept constant, the phase rule for a two component system can be modified as

$$F = C - P + 1$$

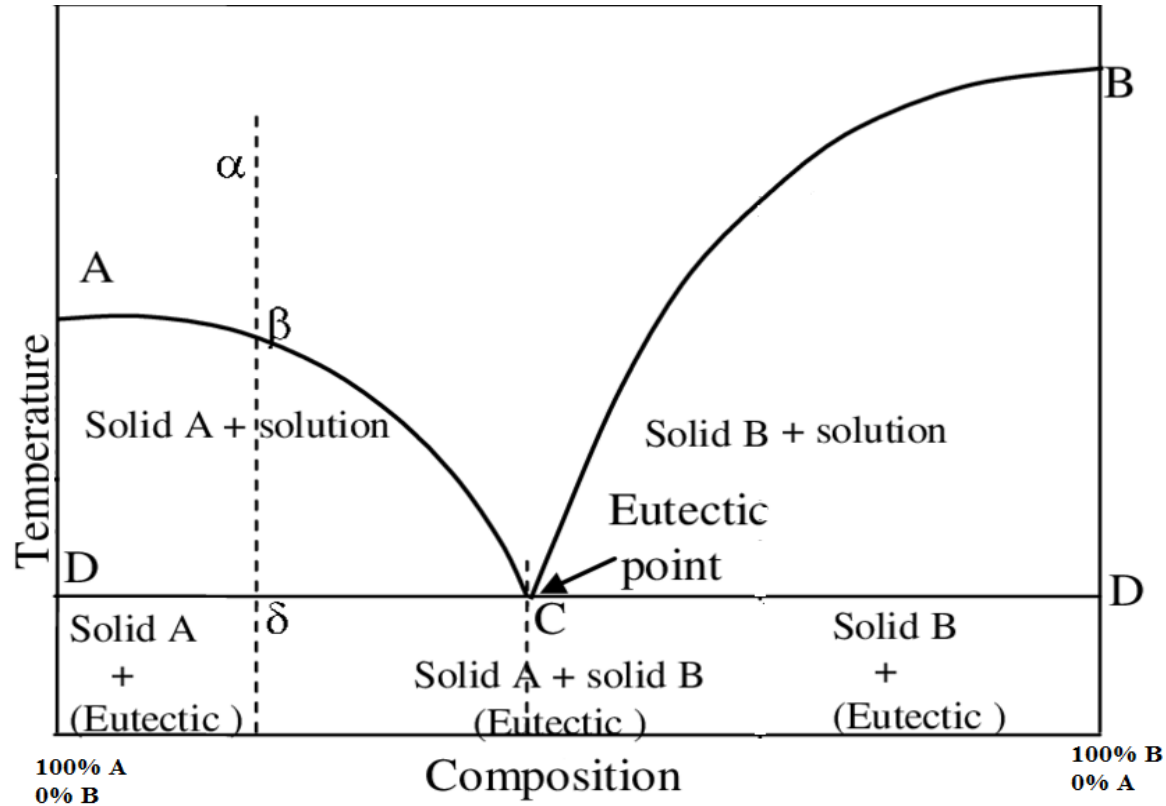
Condensed phase rule or Reduced phase rule.

The two variables in this case are temperature and concentration.

SIMPLE EUTECTIC SYSTEM

A simple eutectic system is a two-component system in which the two components do not form any compound with each other, they are completely miscible in the liquid state and crystallization of any such solution yields either a pure component or an intimate mixture of the two called the eutectic mixture.

It is a temperature-composition diagram.

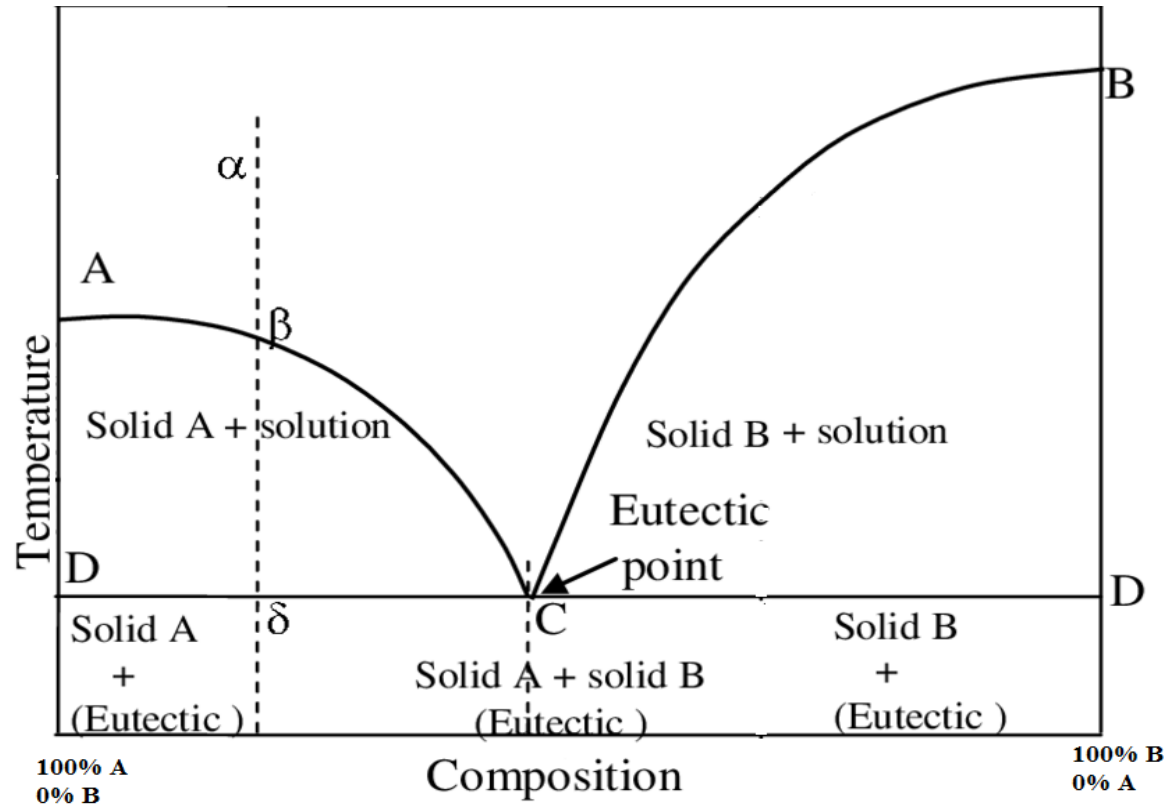


Curves AC and BC:

- Curve AC is the freezing point curve of A. The addition of component B to A, lower that freezing point of A. Along the curve AC, solid A is in equilibrium with solution of B in A.
- Curve BC is the freezing point curve of B. The addition of component A to B, lower that freezing point of B. Along the curve BC, solid B is in equilibrium with solution of A in B.

Curves AC and BC represent two-phase equilibria with one degree of freedom by applying condensed Gibbs phase rule.

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

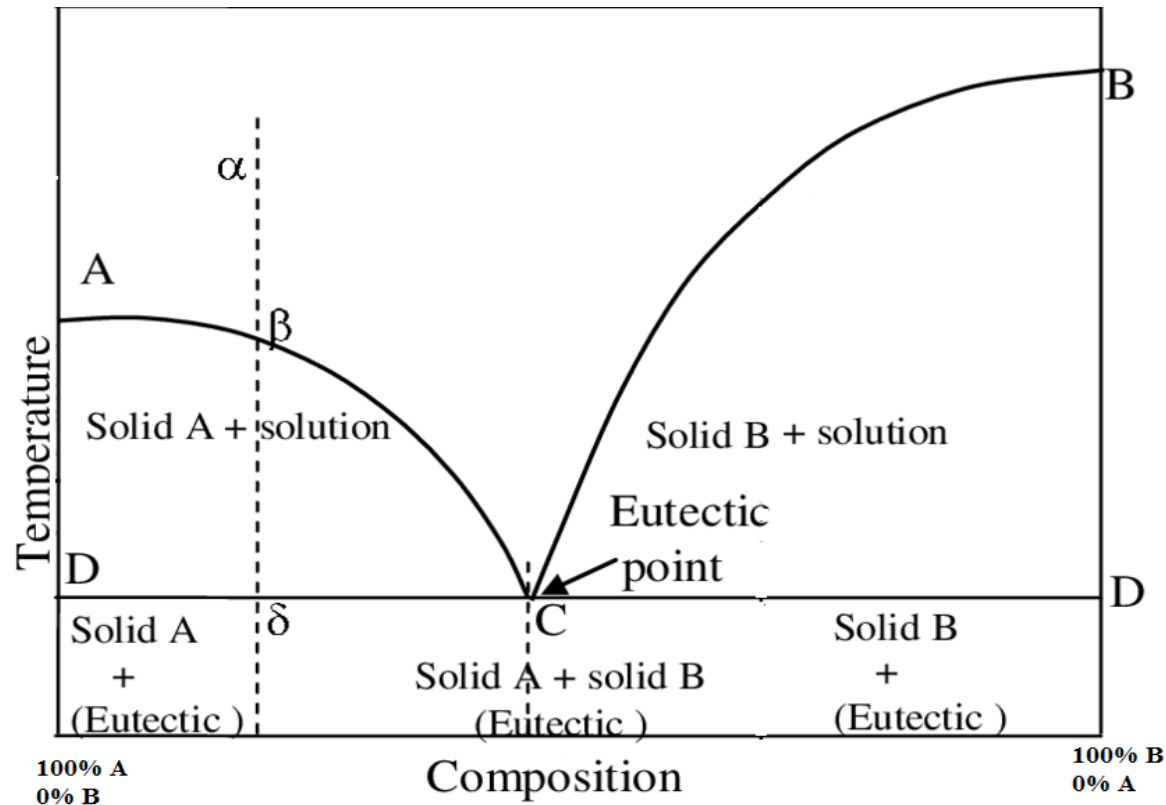


Point C:

- At point C, where solids A and B are in equilibrium with the liquid.
- The point C is called the **eutectic point** and the corresponding composition is called the **eutectic composition** and the temperature corresponding to the eutectic point is called the **eutectic temperature**.
- The composition corresponding to the eutectic point has the lowest melting point.

Since three phases are in equilibrium, point C is an invariant point.

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



A eutectic mixture has a definite composition and a sharp melting point. But it is not regarded as a compound because of the following reasons:

- The two components in it are not in stoichiometric proportions corresponding to any chemical formula.
- Microscopic examination of the mixture reveals the existence of different crystals of the two components.
- An x-ray examination of a eutectic mixture shows two superimposed patterns.

Area above ACB:

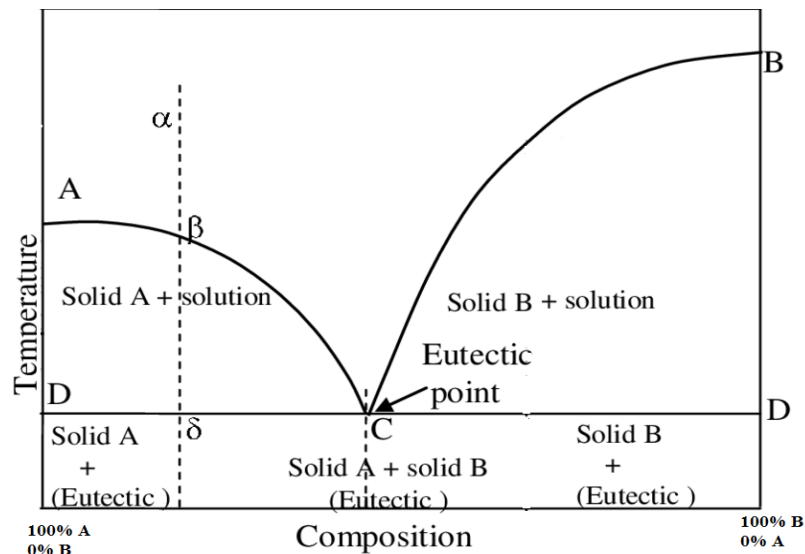
This area represents a homogeneous liquid solution of A and B. There is only one phase and the system is bivariant.

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

Areas within ACD and BCD:

These areas represent the equilibrium between corresponding solid and liquid. Both these areas have two phases and univariant.

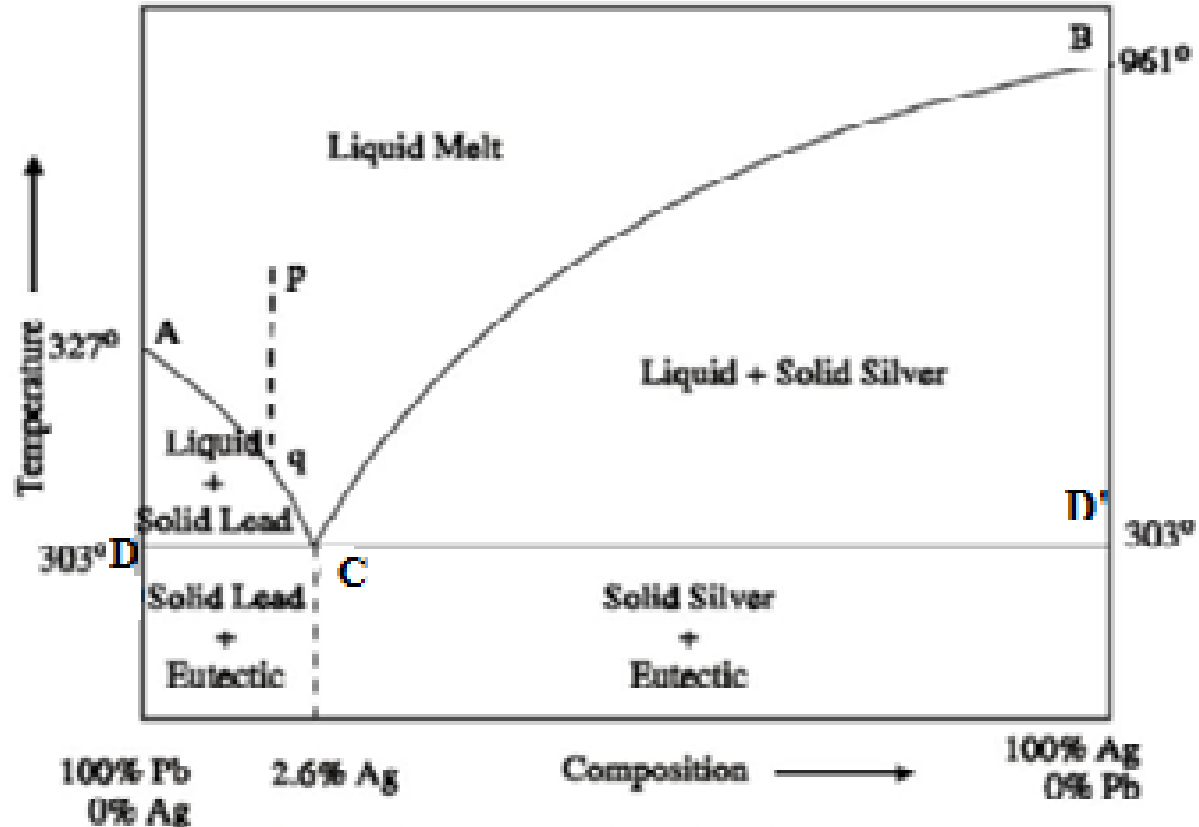
$$F = 2 - 2 + 1 = 1$$



THE LEAD-SILVER SYSTEM:

The Lead-Silver system is studied at constant pressure and the vapour phase is ignored.

Hence the condensed phase rule is used: $F' = C - P + 1$

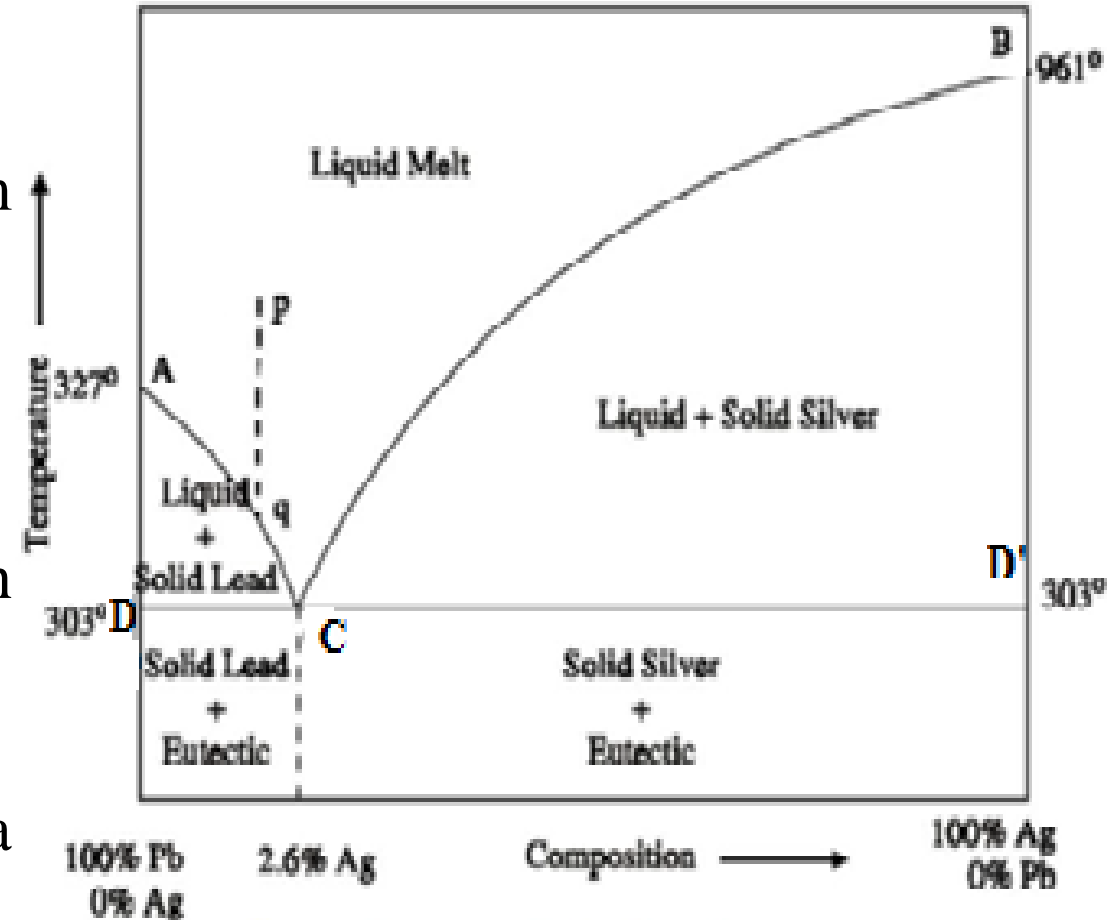


The points A and B represents the freezing points of the pure lead (327 °C) and silver (961 °C) respectively

- Curve AC is the freezing point curve of lead.
- Along the curve AC, solid lead is in equilibrium with solution of silver in lead.
- Curve BC is the freezing point curve of silver.
- Along the curve BC, solid Ag is in equilibrium with solution of Pd in silver.

Curves AC and BC represent two-phase equilibria with one degree of freedom by applying condensed Gibbs phase rule.

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



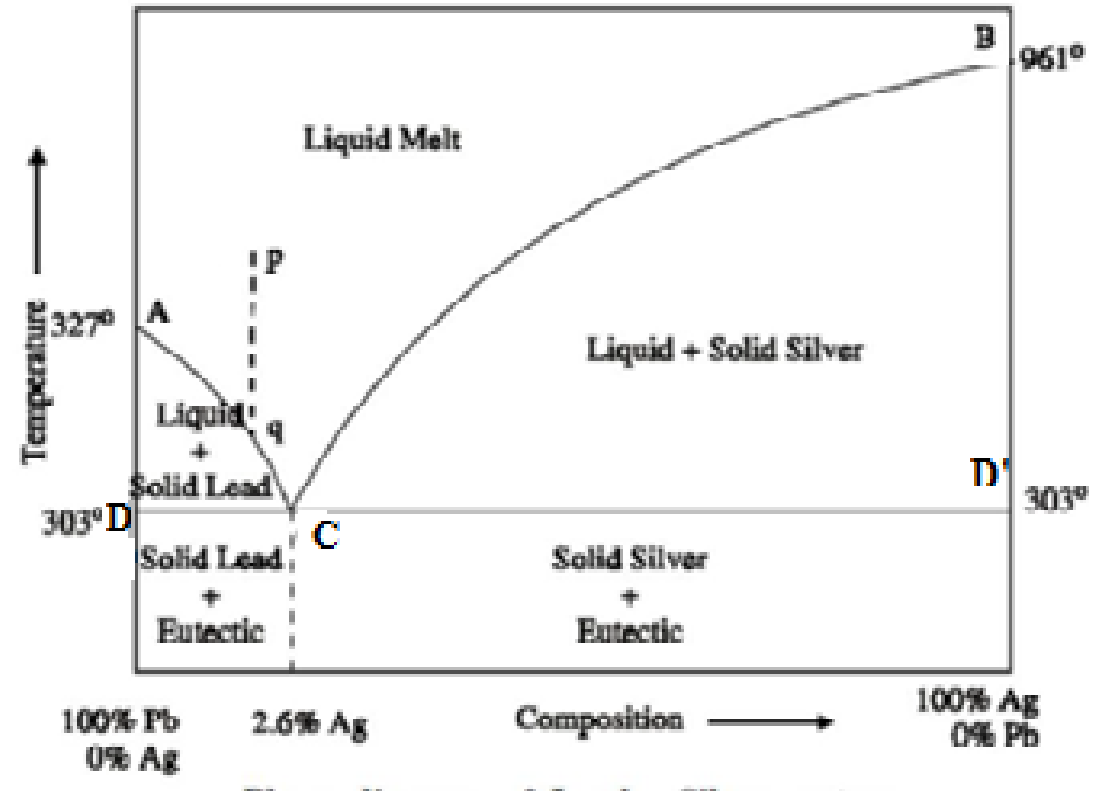
Point C:

- The point C is called the eutectic point
- The eutectic composition (Pb = 97.4% and Ag = 2.6%)
- eutectic temperature (303 °C).

Since three phases are in equilibrium, point C is an invariant point.

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

Below this point the eutectic compound and the metal solidify.



Area above ACB:

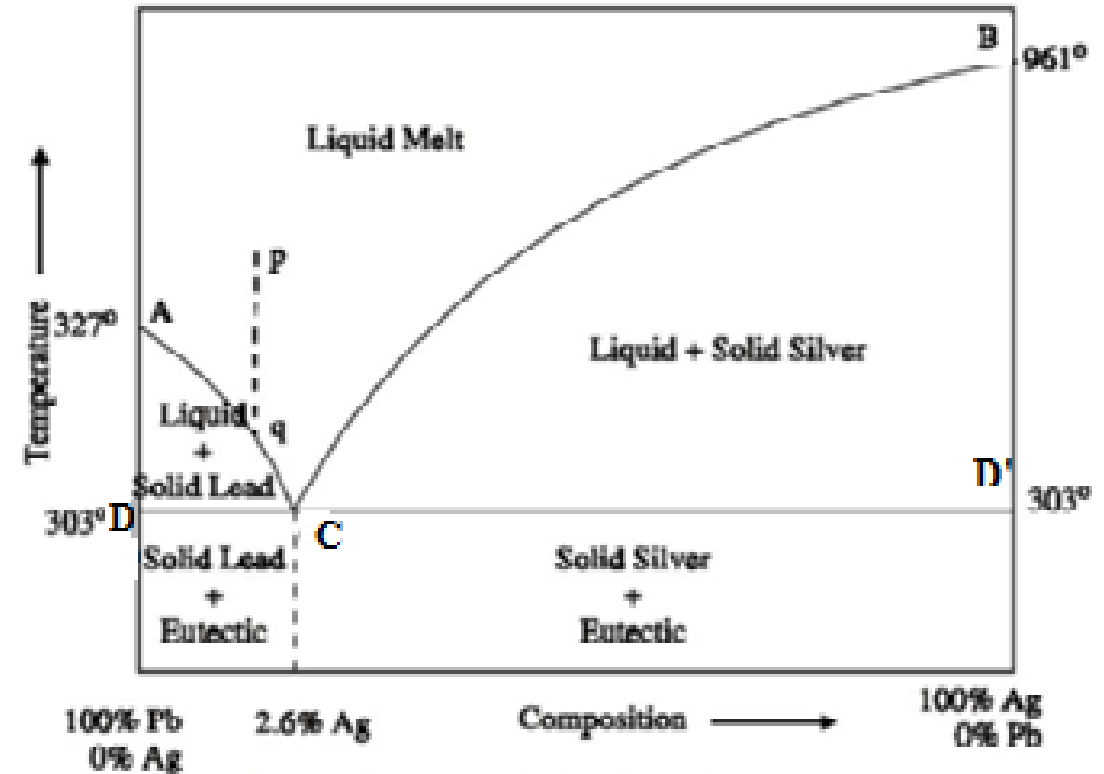
This area represents a homogeneous liquid solution of Pb and Ag. There is only one phase and the system is bivariant.

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

Areas within ACD and BCD:

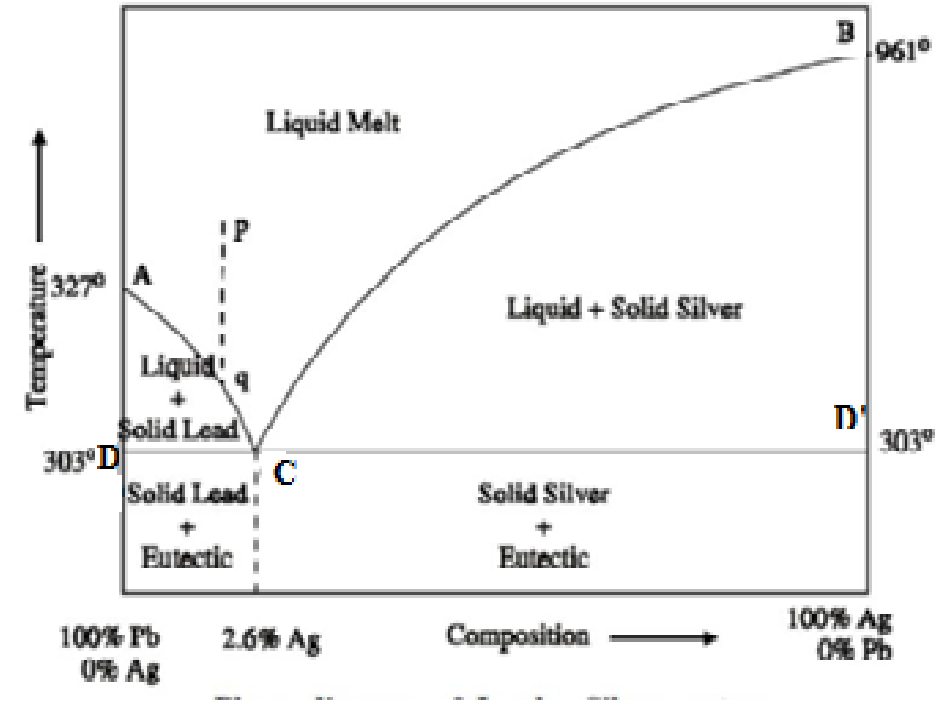
These areas represent the equilibrium between corresponding solid and liquid. Both these areas have two phases and univariant.

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



Pattinson's process - Desilverisation of Argentiferous lead

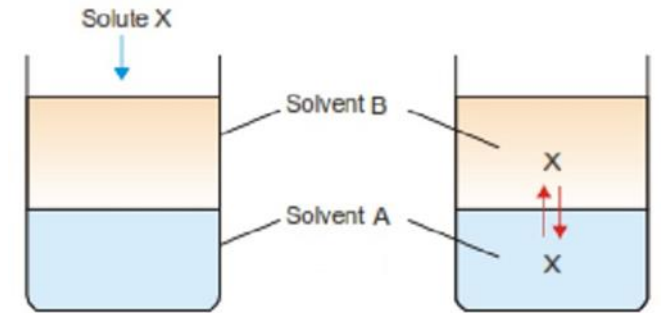
- Argentiferous lead, having a very small amount of silver (say 0.1%), is heated to a temperature above its melting point.
- The system has only the liquid phase represented by the point 'p'.
- It is then allowed to cool where the temperature decreases along the line 'pq'. As soon as the point q is reached, Pb is crystallised out and the solution will contain relatively increasing amounts of Ag.
- On further cooling, more and more of Pb is separated along the line AC. The melt continues to be richer and richer in Ag until the point C is reached, where the percentage of Ag rises to 2.6%.
- The process of raising the relative proportions of Ag in the alloy is known as Pattinson's process.
- Silver can be isolated from the eutectic mixture by means of cupellation.



NERNST'S DISTRIBUTION LAW

A solute distributes itself between two immiscible solvents in such a way that the ratio of the concentrations of the solute in the two solvent will remain constant at a particular temperature.

- This law is one of the laws applying to ideal dilute solutions.
- It was discovered by W. Nernst in 1890.



If a solute X distributes itself between the two immiscible solvents A and B, then we have

$$\frac{\text{Concentration of X in solvent A}}{\text{Concentration of X in solvent B}} = \frac{C_1}{C_2}$$

Where C_1 and C_2 are the concentrations of solute X in solvents A and B respectively.

According to Nernst distribution law

$$\frac{\text{Concentration of X in solvent A}}{\text{Concentration of X in solvent B}} = \frac{C_1}{C_2} = K_D$$

The constant K_D is called the *distribution coefficient or partition coefficient*.

Essential conditions necessary for the validity of the law:

1. Constant temperature
2. Existence of similar molecular species in the two liquid phases, which is in contact with each other.
3. Mutual immiscibility of two solvents.
4. The solutions must be dilute.

When the solute forms saturated solutions in the two solvents, then the partition coefficient K_D may be given as;

$$K_D = \frac{C_1}{C_2} = \frac{S_1}{S_2}$$

Where S_1 and S_2 are the solubilities of solute X in solvents A and B respectively.

APPLICATIONS OF NERNST'S DISTRIBUTION LAW

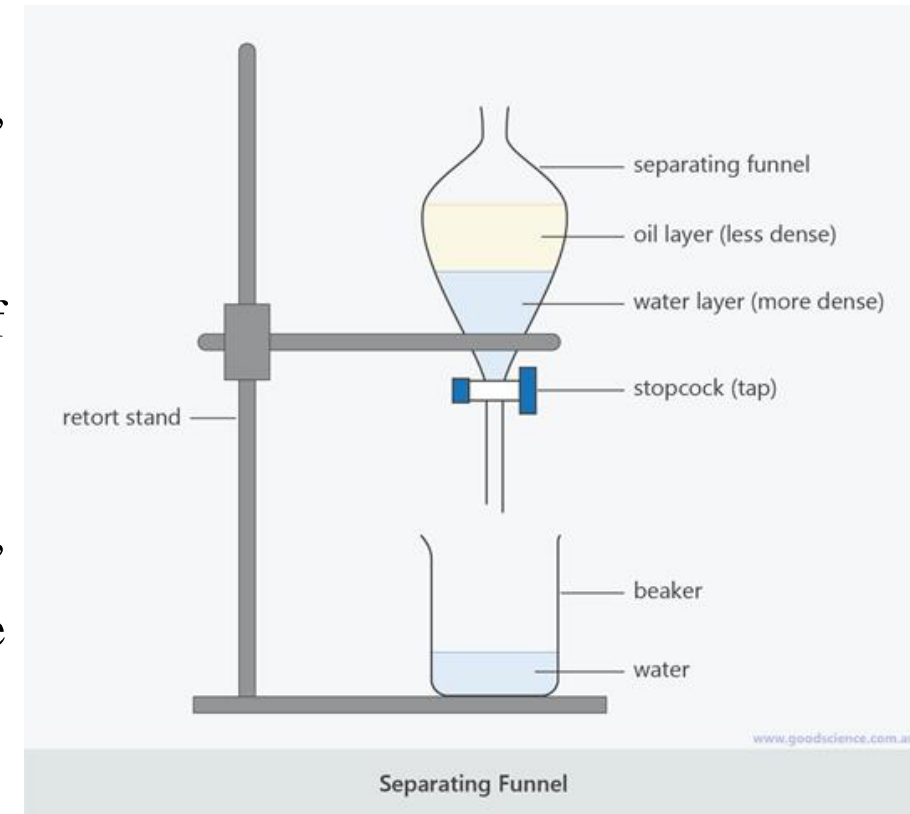
- **Solvent Extraction**
- **Study of Association of Molecules**
- **Study of Dissociation of Molecules**
- **Distribution Indicators**

Solvent Extraction:

- **Solvent extraction** is the process of extracting out a solute from a solvent.
- It is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic **solvent**.

Solvent extraction is based on distribution law:

- The organic solutes are most soluble in organic solvents like ether, benzene etc. than water.
- The distribution ratio of most organic compounds are in favour of organic solvent.
- When an aqueous solution of an organic solute is shaken with ether, most of the solute comes into the ether layer, which can then be separated by evaporation.
- The process of solvent extraction is done by using separating funnel.



It's advantageous to do extraction in successive stages using smaller lots of solvents rather than doing extraction once using the entire lot.

In other words, multiple extraction is more effective than single step extraction.

Proof:

Let 'W' g of the solute is present in 'V' mL of the solution made in solvent A. If 'v' mL of the extracting solvent B is used each time and K_D is the distribution coefficient.

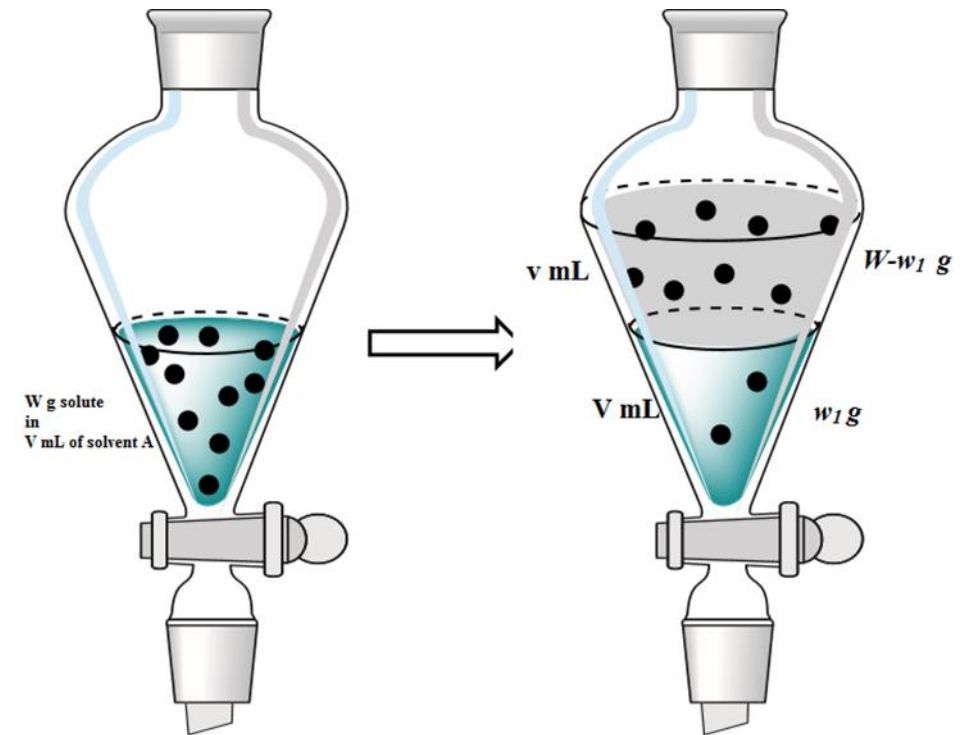
After first extraction with 'v' mL of the extracting solvent B:

w_1 g of the substance left unextracted in solvent A and $(W - w_1)$ g is extracted by 'v' mL of the solvent B.

$$\text{Concentration of solute in solvent A} = \frac{w_1}{V}$$

$$\text{Concentration of solute in solvent B} = \frac{W - w_1}{v}$$

$$K_D = \frac{w_1 / V}{(W - w_1) / v}$$



$$\text{Or, } K_D \cdot V \cdot (W - w_1) = w_1 \cdot v$$

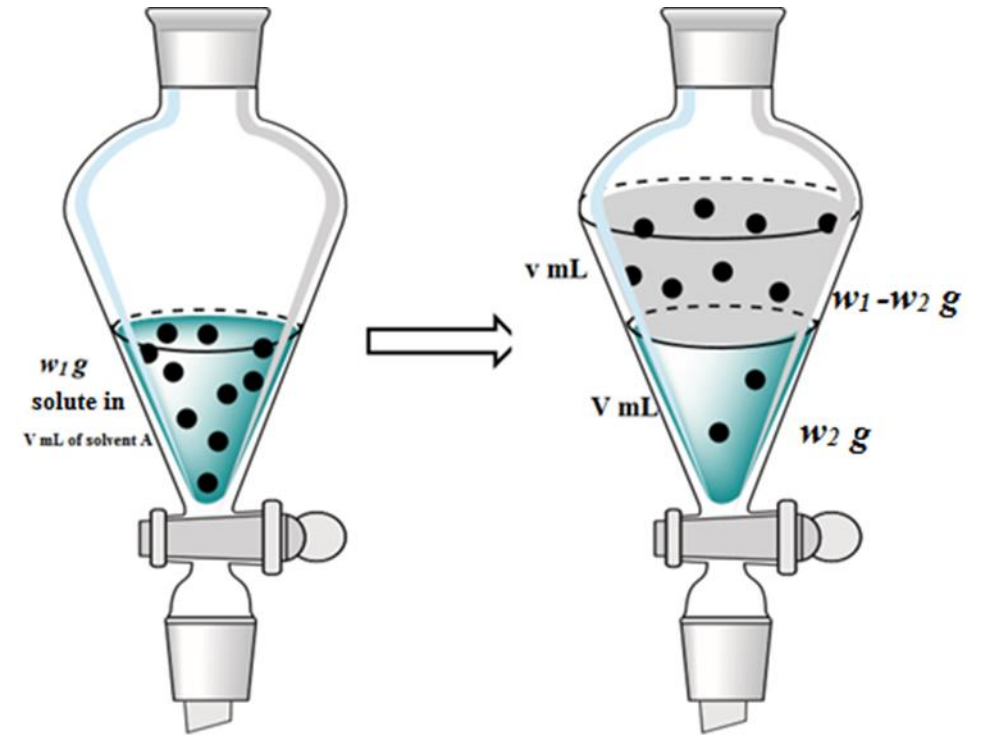
$$\text{Or, } w_1 = \frac{K_D \cdot V}{(v + K_D \cdot V)} W$$

After second extraction with 'v' mL of the extracting solvent B:

w_2 g of the substance left unextracted in solvent A and $(w_1 - w_2)$ g is extracted by 'v' mL of the solvent B.

$$\text{Concentration of solute in solvent A} = \frac{w_2}{V}$$

$$\text{Concentration of solute in solvent B} = \frac{w_1 - w_2}{v}$$



$$K_D = \frac{w_2 / V}{(w_1 - w_2) / v}$$

$$w_2 = \left[\frac{K_D \cdot V}{(v + K_D \cdot V)} \right] w_1$$

Substituting the value of w_1 in the above expression we get,

$$w_2 = \left[\frac{K_D \cdot V}{(v + K_D \cdot V)} \right] \left[\frac{K_D \cdot V}{(v + K_D \cdot V)} \right] W \qquad w_2 = \left[\frac{K_D \cdot V}{(v + K_D \cdot V)} \right]^2 W$$

In general the weight of the solute that remains unextracted (w_n) after 'n' extractions is given by:

$$w_n = \left[\frac{K_D \cdot V}{(v + K_D \cdot V)} \right]^n W$$

In order to make w_n as small as possible, for a given value of K_D , 'n' should be large and 'v' is as small as possible.

The efficiency of extraction increases, if the extraction is carried out in a number of extractions than in a single stage extraction.

STUDY OF ASSOCIATION:

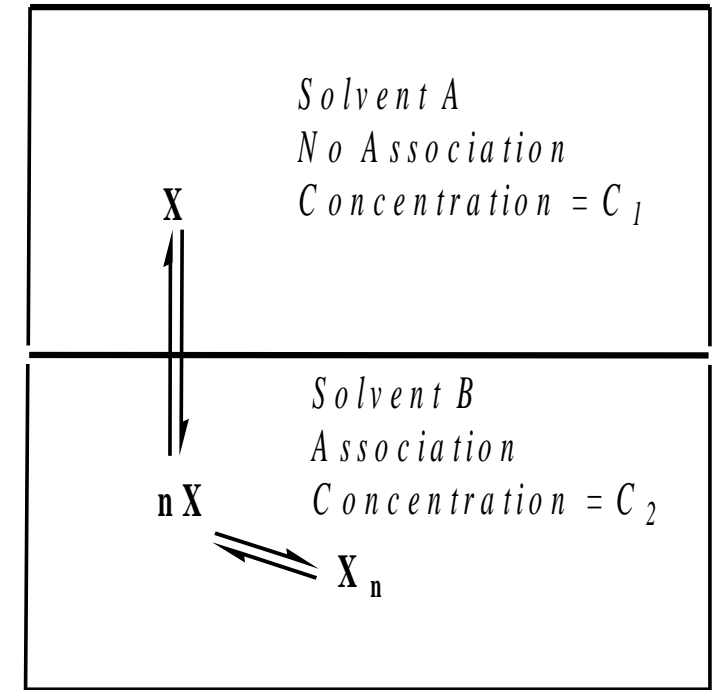
Consider a system of two immiscible solvents A and B. The solute X exists in normal form in solvent A and the solute X undergoes association in solvent B. 'n' is the number of molecules associated to form one associated molecule in solvent B. Then the distribution law is modified as:

$$K_D = \frac{C_1}{\sqrt[n]{C_2}}$$

Where C_1 and C_2 are the concentrations of solute X in solvents A and B respectively.

Using the values of C_1 and C_2 from several experiments on the system and by putting $n = 2, 3, 4, \dots$ the ratio $\frac{C_1}{\sqrt[n]{C_2}}$ is calculated in each case. The value for which the ratio remains constant gives 'n'.

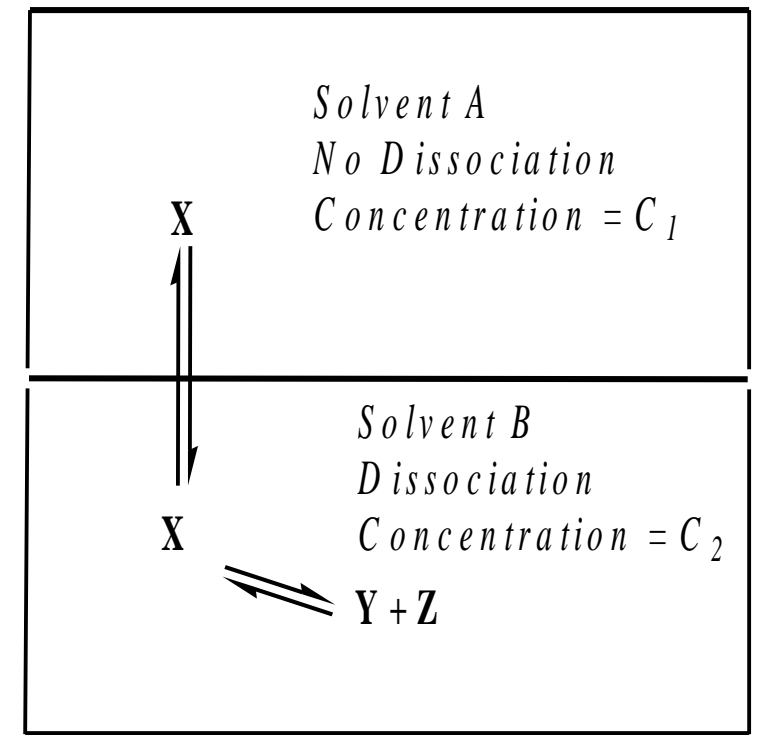
For example: Consider the distribution of benzoic acid in water-benzene system. From the distribution studies 'n' is obtained as 2. Hence benzoic acid exists as dimer in benzene, $(C_6H_5COOH)_2$



STUDY OF DISSOCIATION:

Consider a system of two immiscible solvents A and B. The solute X exists in normal form in solvent A and the solute X undergoes dissociation in solvent B. Then the distribution law is modified as:

$$K_D = \frac{C_1}{C_2(1-\alpha)}$$



Where C_1 and C_2 are the concentrations of solute X in solvents A and B respectively and α is the degree of dissociation of the solute. The value of α can be determined from other experiments for a particular concentration. Then the value of distribution coefficient can be calculated.

For example: this method is used to study the dissociation of weak acids like oxalic acid.

DISTRIBUTION INDICATORS:

- The end point of a titration involving a very dilute aqueous solution may be easily detected by adding a few drops **of a suitable solvent immiscible with water**.
- This becomes possible due to the formation of a distribution system which has a K_D value highly in favour of the new solvent added; it is referred to as a distribution indicator.

Example:

Consider the titration of an extremely dilute aqueous solution of *iodine* against *sodium thiosulphate* solution. If a few drops of **CS₂** are added to the iodine solution, most of the iodine passes into the CS₂ layer giving it a deep violet colour. This occurs because, for the distribution of iodine between CS₂ and water, K_D is very high (~400) in favour of CS₂.

- The end point of the above titration is therefore easily detectable in the form of the disappearance of the violet colour. Thus **CS₂ as a distribution indicator**. CCl₄ can also act in a similar manner for the above titration.