

# Phase Equilibria

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# The Phase Rule



- ❖ It was first presented by **Gibbs** in 1875.
- ❖ It is very useful to understand the effect of intensive variables, such as temperature, pressure, or concentration, on the equilibrium between phases as well as between chemical constituents.
- ❖ It is used to deduce the number of degrees of freedom (***f***) for a system. Sometimes called: “*the variance of the system*”.

**It states that :**

When the equilibrium between any number of phases is influenced only by temperature, pressure and concentration but not influenced by gravity, or electrical or magnetic forces or by surface action then the number of Degrees of Freedom (**F**) of the system is related to the number of Components (**C**) and of Phases (**P**) by the phase rule equation:

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

# Phase Equilibria

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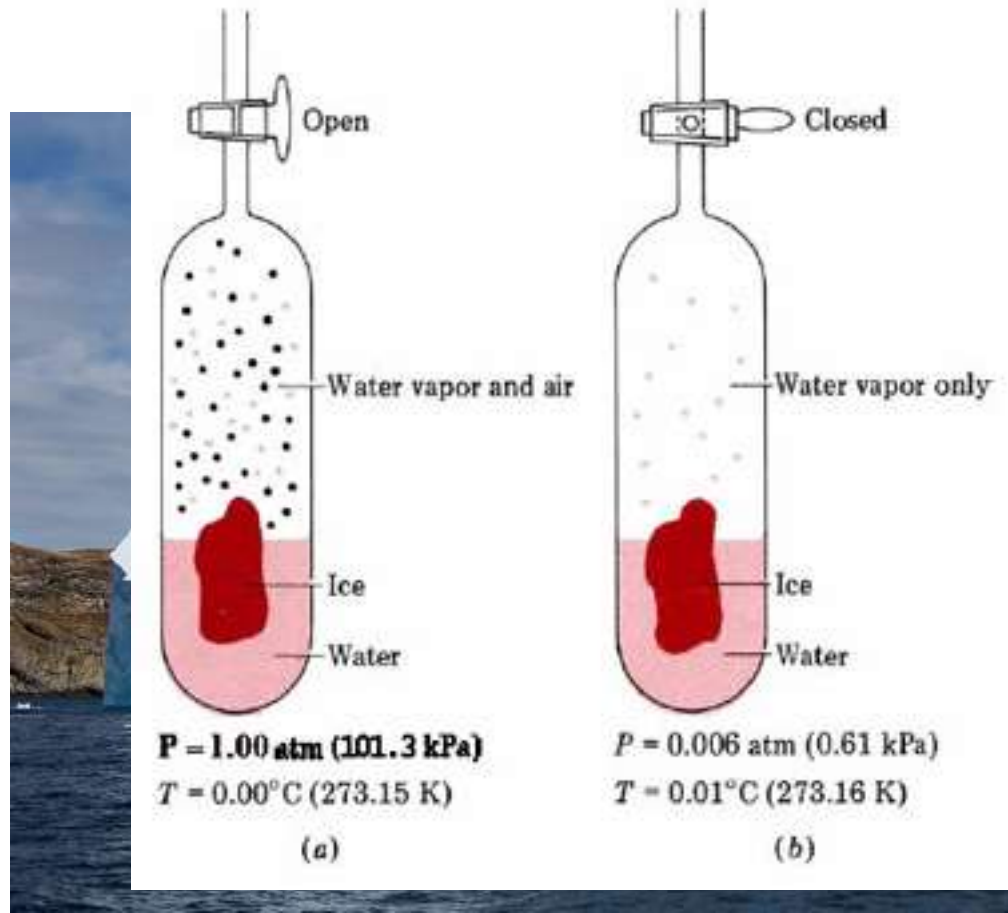
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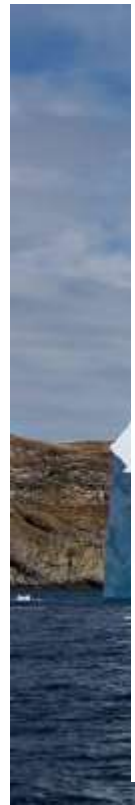
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# Explanation of the Term 'Phase'

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### Homogeneous and Heterogeneous Equilibria

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(6) **Mixture**

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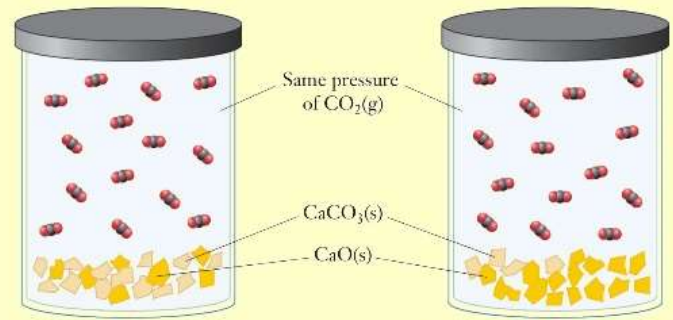
properties.

(ii) **A mi**

Each of these substances having different physical and phase. Thus a mixture of calcium carbonate ( $\text{CaCO}_3$ ) a phases.

Let us consider the equilibrium system: the **Decomp** calcium carbonate is heated in a closed vessel, we have ;  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$

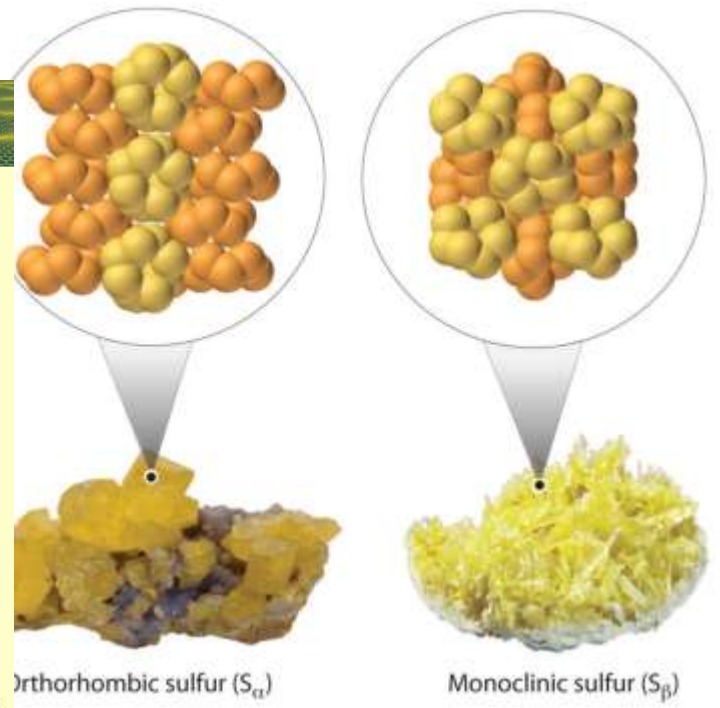
There are two solid phases and one gas phase. Hence it is a 3-phase system.



Much  $\text{CaCO}_3(s)$ , little  $\text{CaO}(s)$

Little  $\text{CaCO}_3(s)$ , much  $\text{CaO}(s)$

- For the decomposition reaction of  $\text{CaCO}_3(s)$  forming  $\text{CaO}(s)$  and  $\text{CO}_2(g)$ , the equilibrium constant only depends on the  $\text{CO}_2$  concentration because  $\text{CaCO}_3$  and  $\text{CaO}$  are solids.



Orthorhombic sulfur ( $S_\alpha$ )

Monoclinic sulfur ( $S_\beta$ )



# Explanation of the Term 'Component'

The term **component** is 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.**

A system ' $C$ ' in the *Phase Rule equation* stands for the number of components of a system in equilibrium.

**(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.





**(1) Water and sulphur systems are 1-component systems.**

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

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

**(2) Mixture of gases.**


A mixture of gases, say  $O_2$  and  $N_2$ , constitutes one phase only. Its composition can be expressed by two chemical substances  $O_2$  and  $N_2$ . Hence, a mixture of  $O_2$  and  $N_2$  has two components.

**Phase**

**Components**

Gaseous Mixture =

$x O_2 + y N_2$



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

**Phase**

**Components**

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

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 phases, namely **aqueous solution** and **solid sodium chloride**. The composition of both phases can be expressed in terms of two chemical individuals NaCl and H<sub>2</sub>O.

**Phase**

**Components**

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

Solid sodium chloride =  $\text{NaCl} + 0 \text{H}_2\text{O}$

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

Let us select calcium oxide (CaO) and carbon dioxide (CO<sub>2</sub>) as the components. Then we can write,

Phase		Components
CaCO <sub>3</sub>	=	CaO + CO <sub>2</sub>
CaO	=	CaCO <sub>3</sub> – CO <sub>2</sub>
CO <sub>2</sub>	=	CaCO <sub>3</sub> – CaO

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**.



## Dissociation of $\text{NH}_4\text{Cl}$ ???

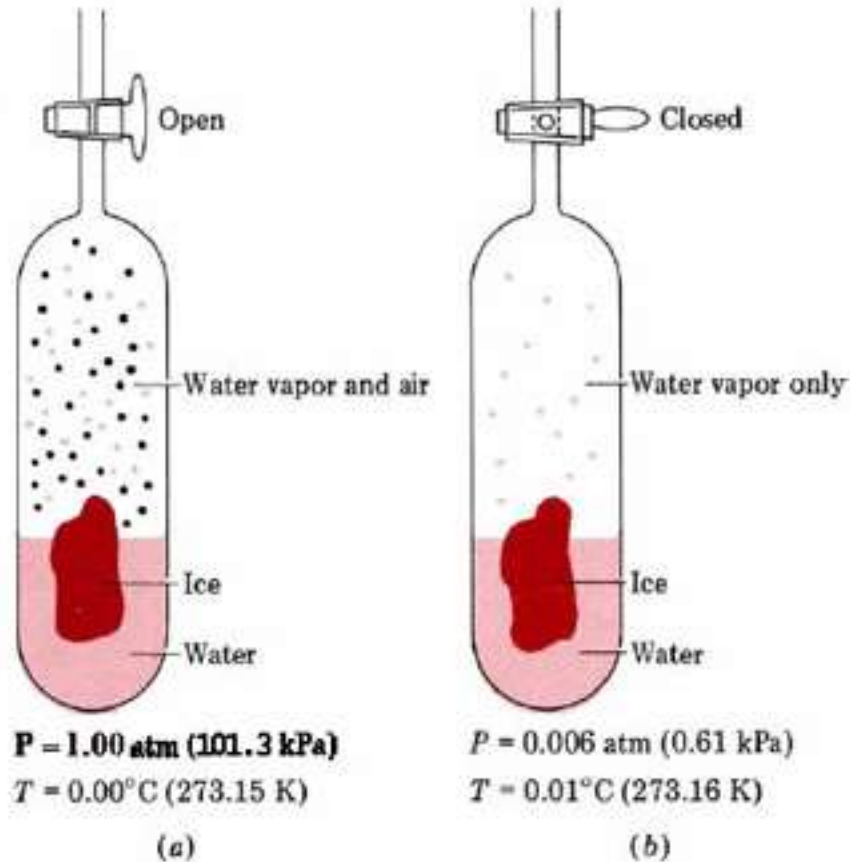


# Degrees of Freedom

The term  $F = C - 1$  (concentration) the remaining completely

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**For ice-water**  
three phase  
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both the  
automatically, there being no need to specify any variable. Hence **it has no degree of freedom ( $F = 0$ ).**



the phase Rule equation  
number of variable factors  
must be specified so that  
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degree of freedom.  
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degrees of freedom.

$\Rightarrow$  water  $\rightleftharpoons$  vapor, the  
var. Since the freezing  
point of water has also a  
(temperature and pressure) and  
is completely defined  
variable. Hence **it has no**



**For water - water vapor,  $F = 1$ .** The system in which water is in equilibrium with water vapor, has two variables *temperature* and *pressure*. At a definite temperature the vapor 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 ( $F = 1$ ).**

**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 ( $F = 2$ ).**

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

# Derivation of the Phase Rule

Consider a heterogeneous system in equilibrium made of  $C$  components, in which  $P$  phases are present.

We have to determine the degrees of freedom of this system *i.e.*, the number of variables which must be arbitrarily fixed in order to define the system completely. Since the state of the system will depend upon the temperature and the pressure, these *two variables* are always there. The concentration variables, however, depend upon the number of phases.

In order to define the composition of each phase, it is necessary to specify the concentration of  $(C - 1)$  constituents of each phase, the concentration of the remaining component being determined by difference. For  $P$  phases, therefore, the total number of concentration variables will be  $P(C - 1)$  and these along with the two variables mentioned above *viz.*, temperature and pressure, make the total number of the variables of the system equal to  $[P(C - 1) + 2]$ .

Again, for a single component in  $P$  phases there would be  $(P-1)$  dependent variables. And for  $C$  components total number of dependent variables would be equal to  $C(P-1)$ .

Now, degrees of freedom ( $F$ ) = total number of variables – total number of dependent variables

$$\begin{aligned} &= \{P(C - 1) + 2\} - \{C(P-1)\} \\ &= PC - P + 2 - PC + C \\ &= C - P + 2 \end{aligned}$$

# Degrees of freedom for one-component system

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

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

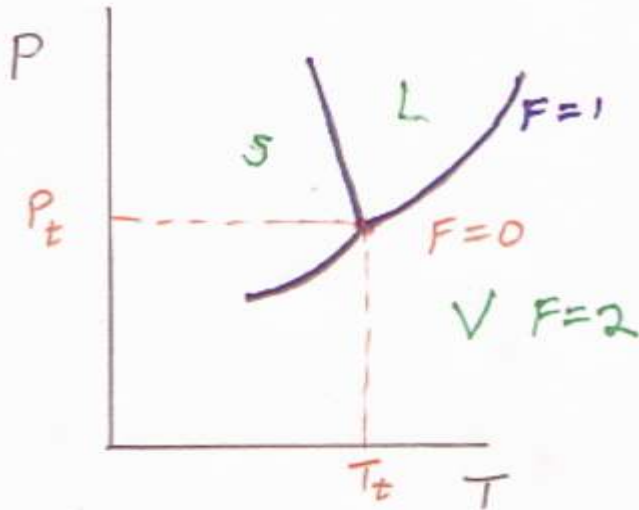
Three cases may arise:

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

$$F = 3 - 1 = 2$$

Thus the system is **bivariant**. It can be completely defined by specifying the two variables, temperature and pressure. Or that, both the temperature and pressure can be varied independently.

Therefore a **single phase** is represented by an **area** on P-T graph.



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

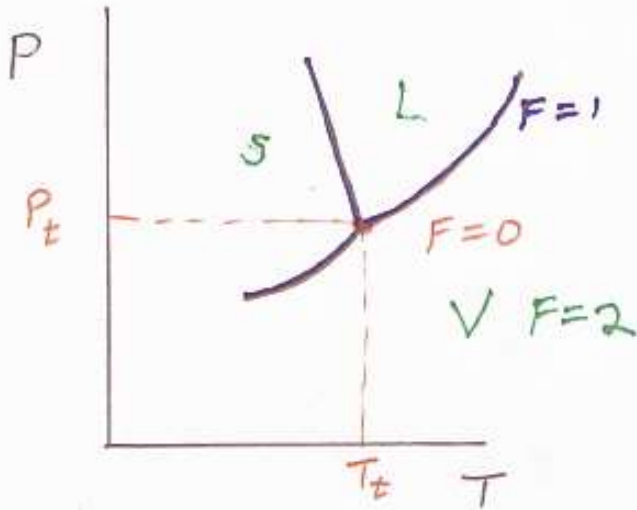
$$F = 3 - 2 = 1$$

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

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

$$F = 3 - P = 3 - 3 = 0 \text{ / Or, } F = 0$$

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



# Triple Point

The triple point of a substance is the **temperature** and **pressure** at which the three phases (gas, liquid and solid) of that substance coexist in thermodynamic equilibrium.

For example, the triple point of mercury occurs at a temperature of  $-38.83^{\circ}\text{C}$  and a pressure of  $0.2\text{ mPa}$ . Triple point of water is  $273.16\text{ K}$  at  $611.2\text{ Pa}$  ( $0.0098^{\circ}\text{C}$  at  $4.58\text{ mm of Hg}$ )

A triple point shows the conditions under which all three phases can coexist in equilibrium. Thus, the system at the triple point may be represented as:



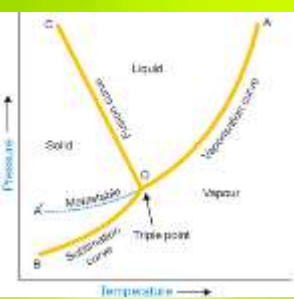
Applying the phase rule equation we have-

$$\begin{aligned} F &= C - P + 2 \\ &= 1 - 3 + 2 \\ &= 0 \end{aligned}$$

This predicts that the system has no degree of freedom at its triple point.



# Phase Diagram



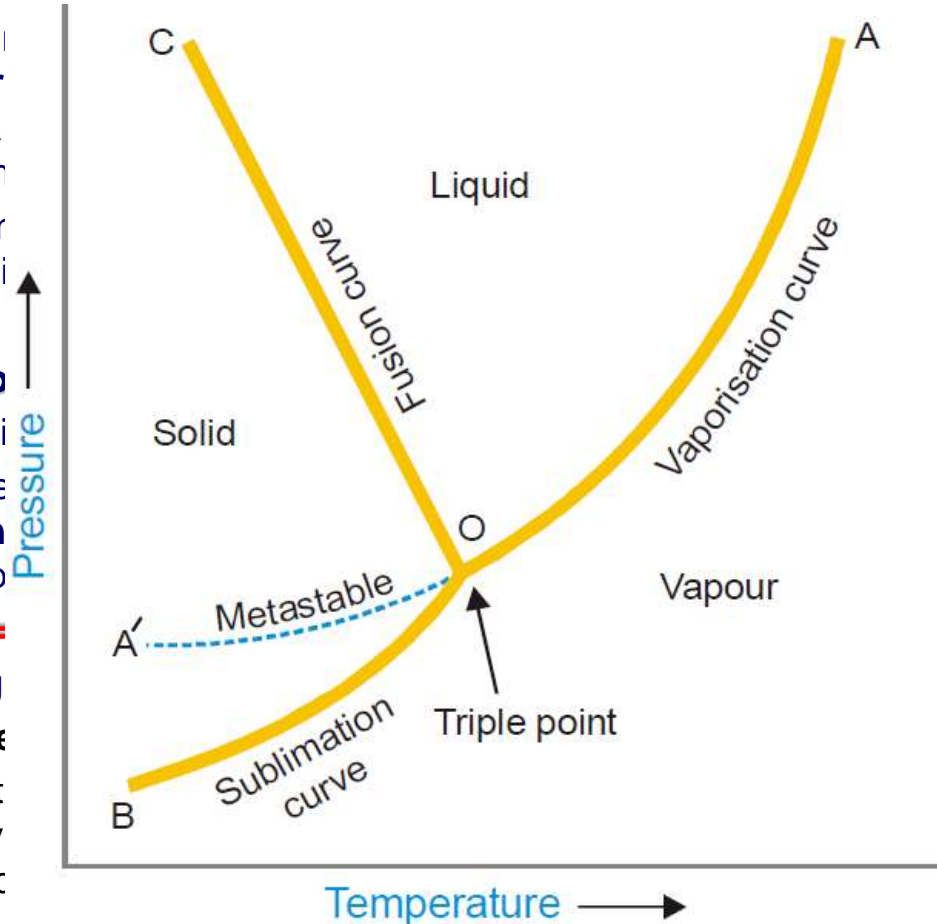
A phase diagram which two or **Figure 1** is a (a) the Region The significant diagram are di

## (1) Regions of

The diagram is 'solid', 'liquid', and 'vapor'. These the condition Applying the p

$F = 1 - 1 + 2 =$  i.e., each sing

Thus each are one of the t independently the condition c



and temperature under dynamic equilibrium. The diagram consists of: it. (triple point) of a phase

'solid', 'liquid', and the three areas shows active phase can exist. We have

conditions wholly within (temperature) can be varied before in order to define d.

## (2) Lines or Curves

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

(a) Solid/liquid line (OC) which represents the equilibrium  $Solid \rightleftharpoons Liquid$ , is referred to as the **Melting curve** or **Fusion curve**.

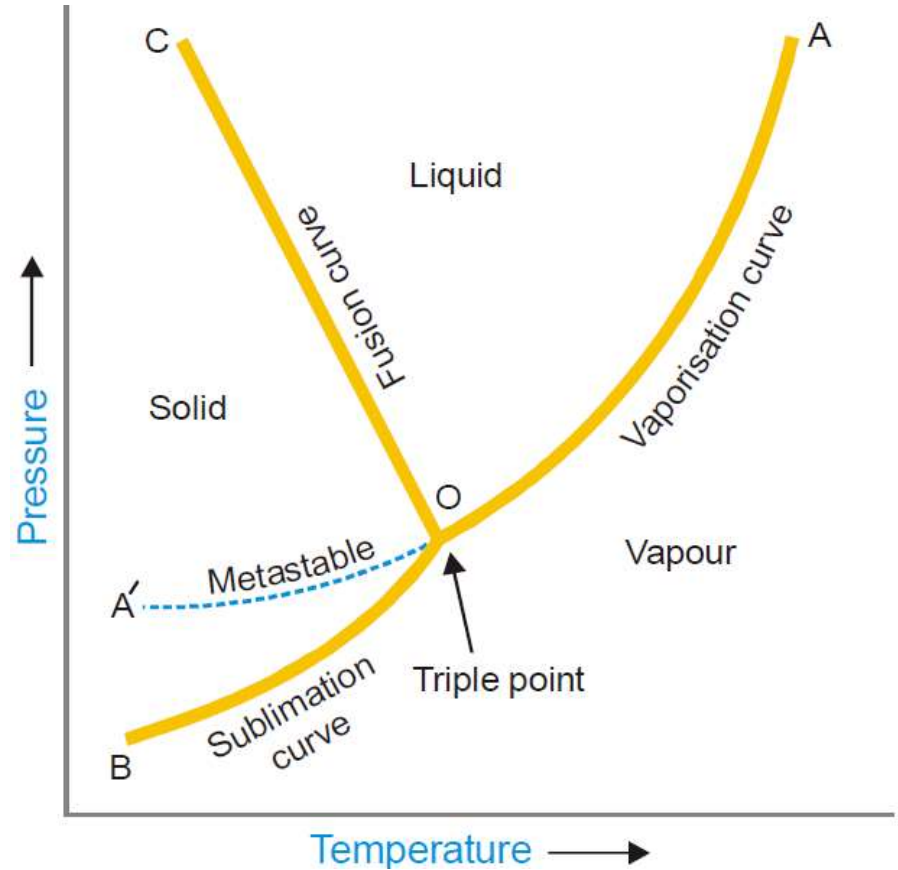
(b) Liquid/vapour line (OA) which represents the equilibrium  $Liquid \rightleftharpoons Vapour$ , is referred to as the **Vapour Pressure curve** or **Vaporisation curve** for the liquid.

(c) Solid/vapour line (OB), which represents the equilibrium  $Solid \rightleftharpoons Vapour$ , is referred to as the **Sublimation curve**.

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

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

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



### (3) Triple Point

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

Thus the system at the triple point may be represented as :

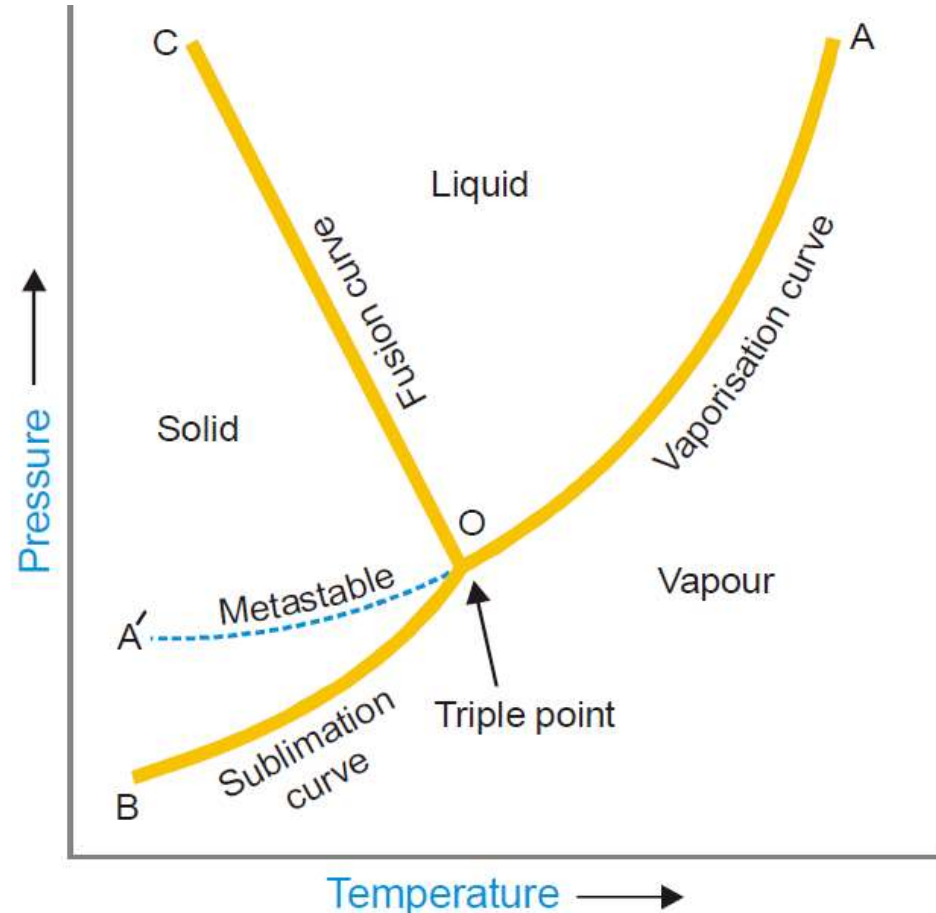


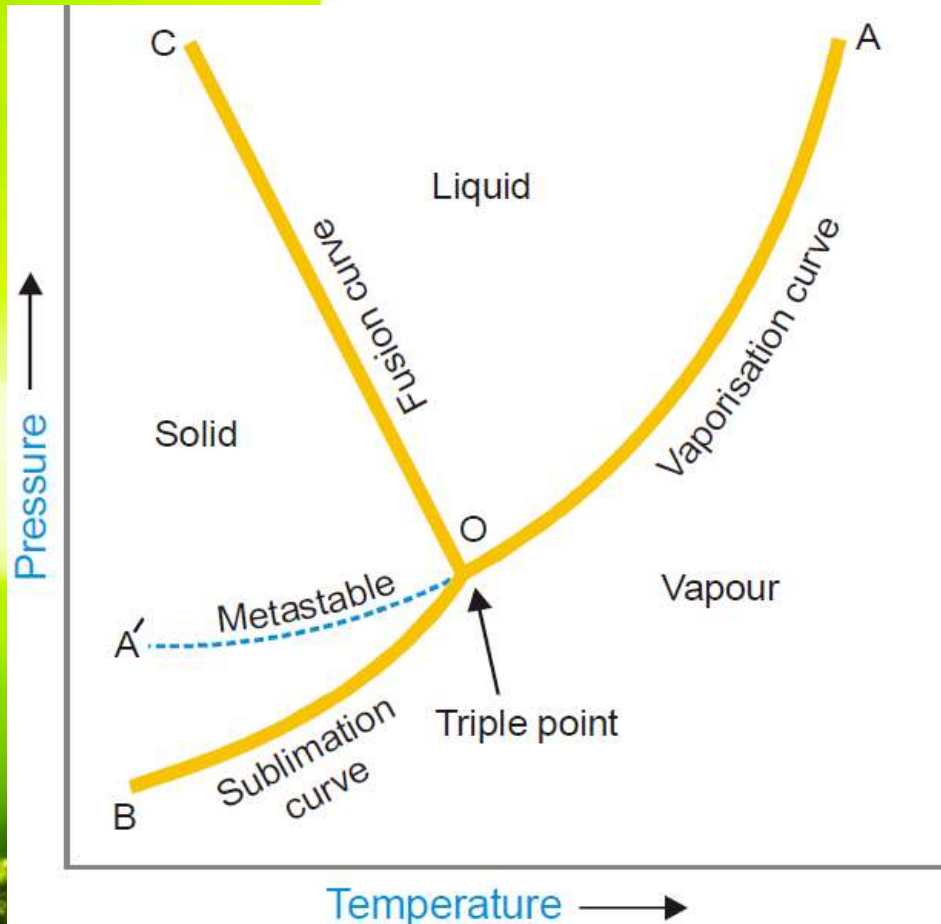
Applying the phase rule equation, we have

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

that means the system has no degree of freedom.

e.g. In water system, the temperature and pressure for the triple point are  $0.0098^{\circ}\text{C}$  and  $4.58 \text{ mm Hg}$  respectively.





## Metastable Equilibrium

The vapour pressure curve AO terminates at the point O, when the liquid freezes or solidifies. However by careful cooling of the liquid under conditions that crystals do not form, the curve AO can be extended to A'. In that case this state is called supercooled' state. The supercooled liquid is in an unstable condition. On a slightest disturbance the entire liquid solidifies rapidly, and the dashed curve OA' represents a **metastable equilibrium**,

Supercooled Liquid  $\rightleftharpoons$  Vapour

This system at once reverts to the true stable system

Solid  $\rightleftharpoons$  Vapour

# The Water System

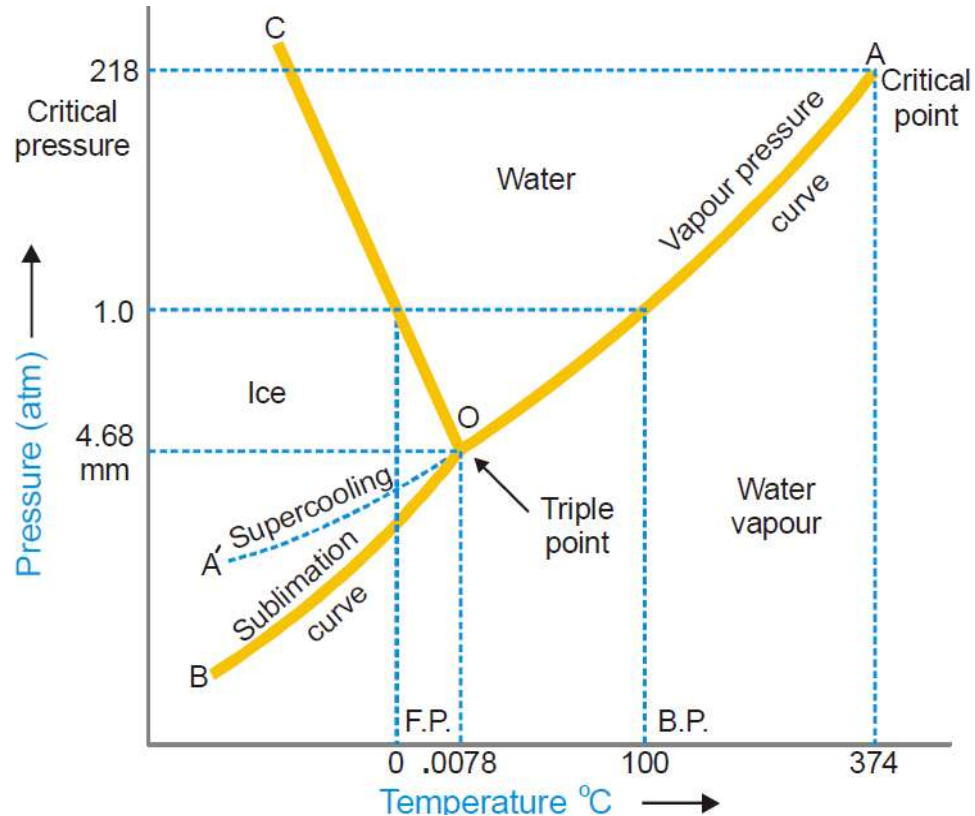
'Water' is a **three-phase, one-component system**. The total number of phases which can exist in equilibrium any time depends on the conditions of temperature and pressure. The phase diagram or  $P$ - $T$  graph of the system/ water/ice/vapour is shown in Figure The **salient features of the phase diagram** are listed below.

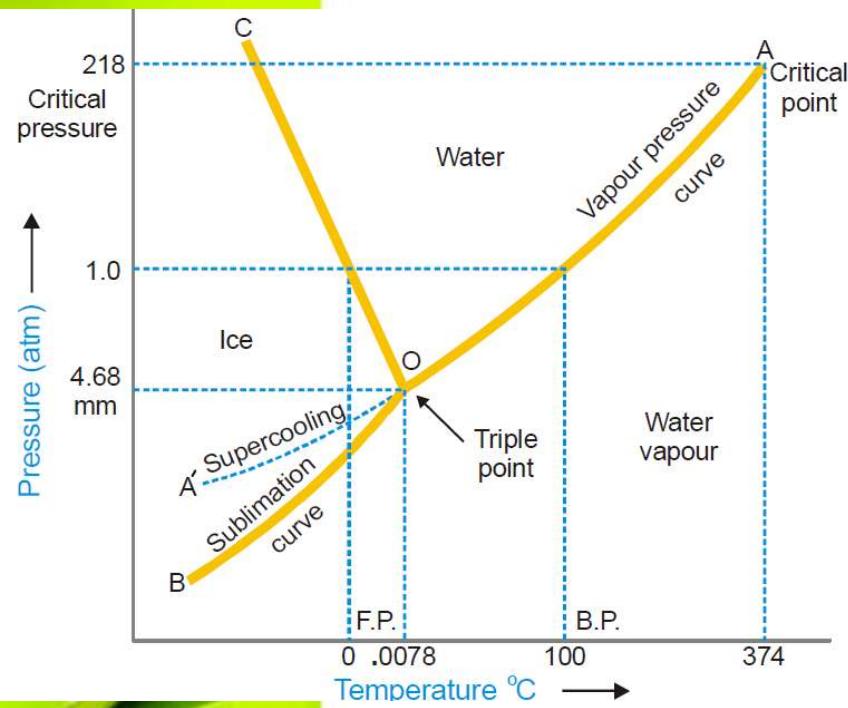
- (1) The Curves  $OA$ ,  $OB$ ,  $OC$**
- (2) The Triple Point  $O$**
- (3) The Areas  $AOC$ ,  $AOB$ ,  $BOC$**

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

## (1) The Curves $OA$ , $OB$ , $OC$

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





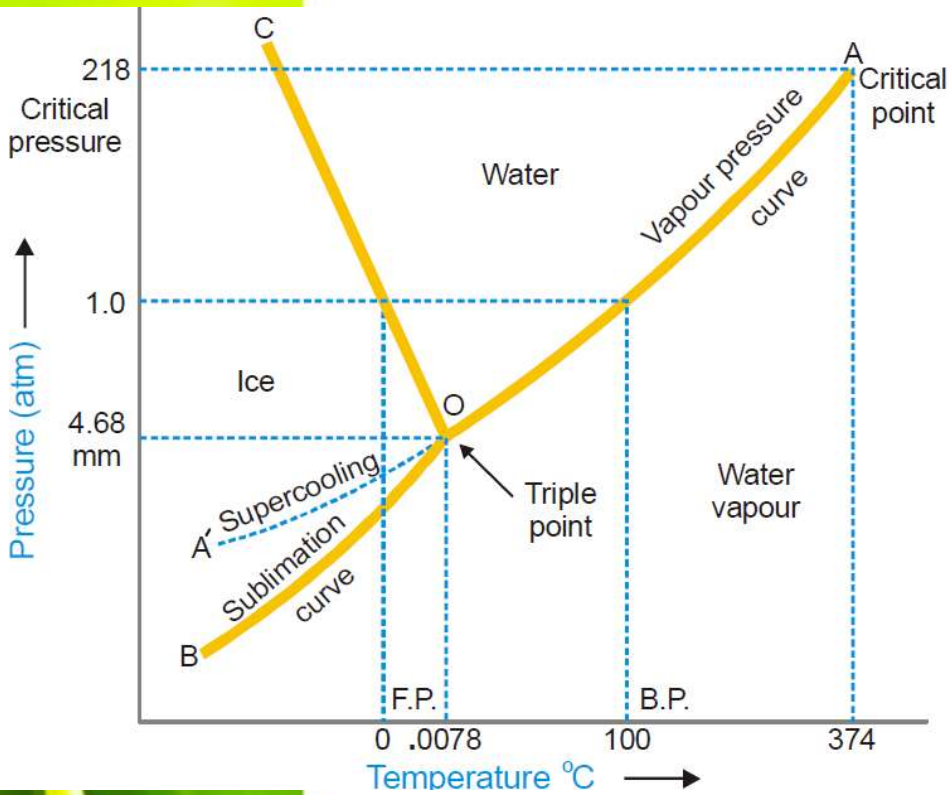
## Curve OA, the Vapour Pressure curve of Water.

It represents the vapour pressure of liquid water at different temperatures. The two phases *water* and *water vapour* coexist in equilibrium along this curve. The curve OA terminates at A, the critical point (218 atm, temp. 374°C) at this point the liquid and vapour are indistinguishable from each other

## Curve OB, the Sublimation curve of Ice.

It shows the vapour pressure of solid ice at different temperatures. The two phases *solid ice* and *vapour* coexist in equilibrium along this curve. The curve terminates at the point B, where no vapour exists.





### Curve OC, the Fusion curve of Ice.

It depicts the effect of pressure on the melting point of ice.

Here *ice* and *water* coexist in equilibrium. The OC slopes to the left indicates the melting point of ice decreases with increase of pressure.

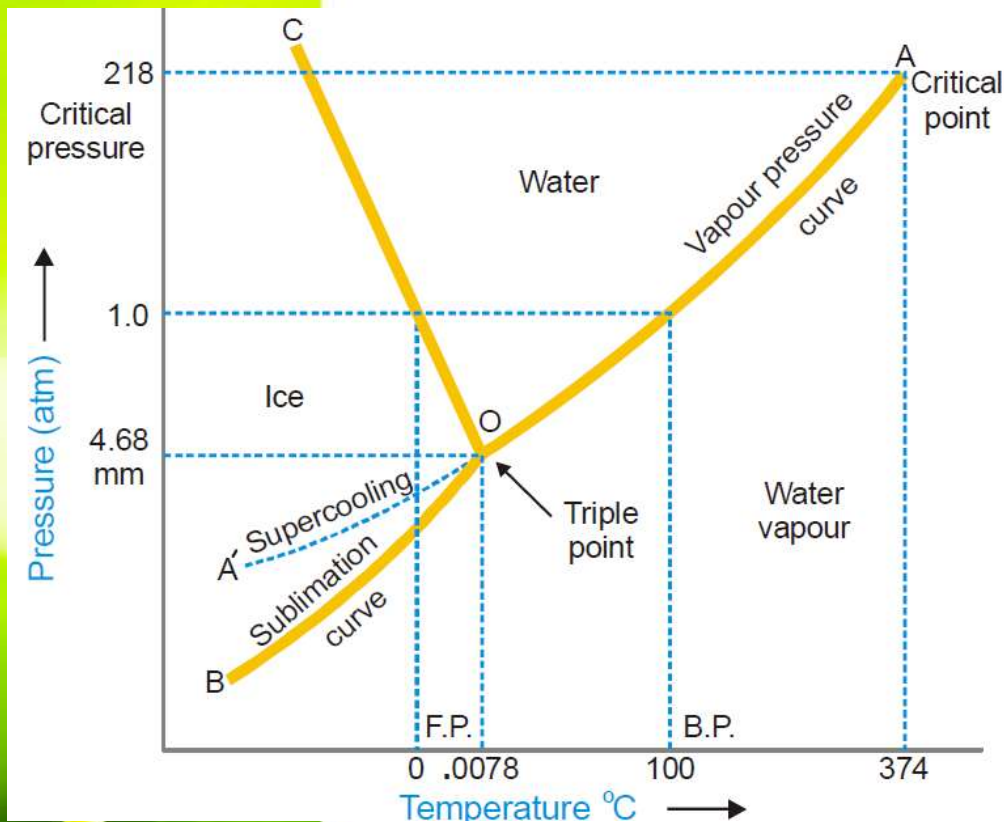
Along the curves OA, OB, OC there are two phases in equilibrium and one component. Therefore,

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

Hence each two-phase system :

water/water vapour represented by OA

ice/water vapour represented by OB  
 ice/water represented by OC has one degree of freedom *i.e.*, is **monovariant**.



## (2) The Triple point 'O'

The curves OA, OB and OC meet at the triple point 'O' where all the three phases *liquid water/ ice/vapour* are in equilibrium.

This occurs at  $0.0078^{\circ}\text{C}$  and vapour pressure  $4.58 \text{ mm Hg}$ . Since there are three phases and one component,

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

i.e., the system at the triple point is **nonvariant**.

## (3) Area AOC, AOB, BOC

Within the areas a single 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**.

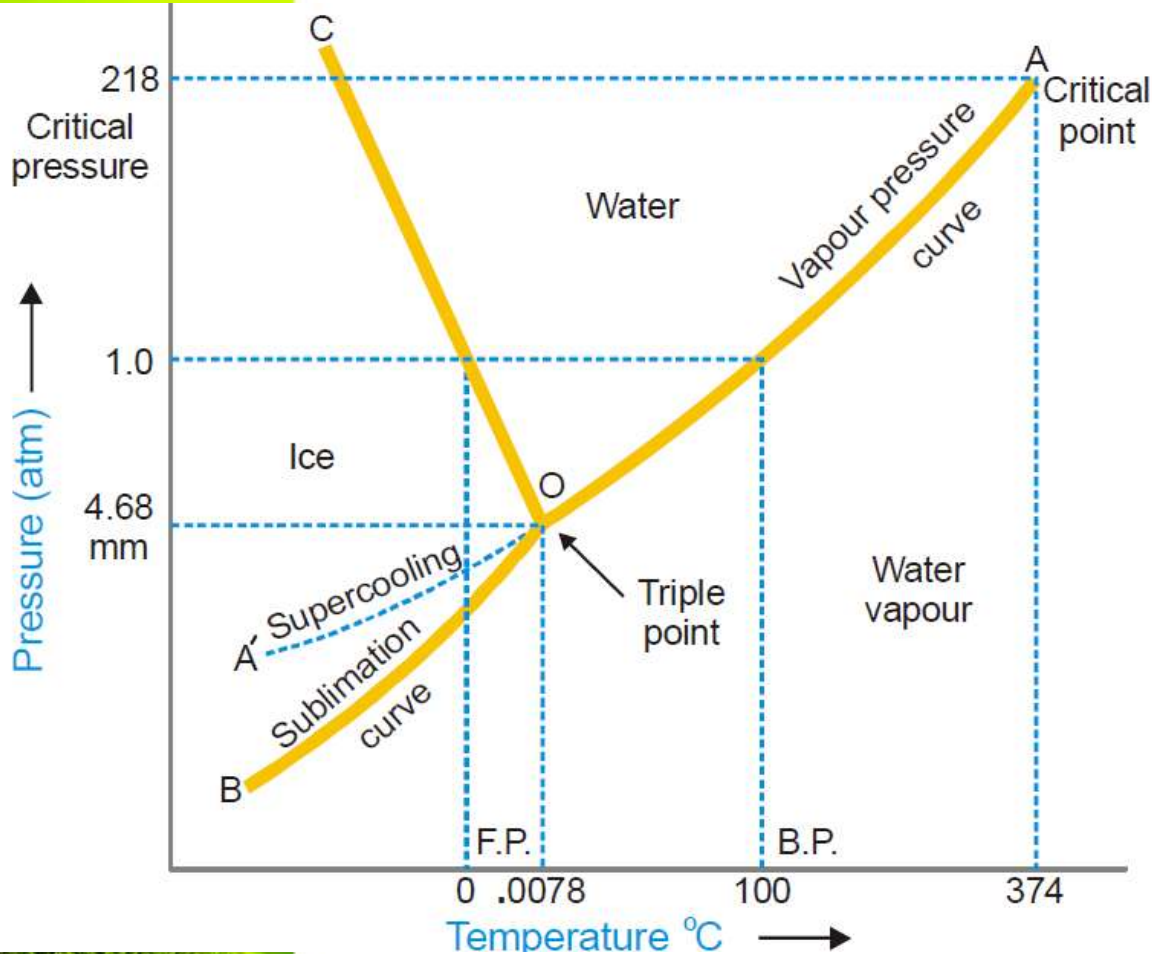
**Area BOC** represents conditions for the one-phase system **ice**.

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

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

Thus the system is **bivariant**.





## (4) Metastable system : Super cooled Water/Vapour System

The vapour pressure curve  $AO$  can be continued beyond the triple point  $O$  as shown by the dashed line  $OA'$ . That is, water can be *supercooled*.

The supercooled water/vapour system is metastable (unstable).

It at once reverts to the stable system ice/vapour on the slightest disturbance or introducing a crystal of ice.

# THE SULPHUR SYSTEM

It is a **one-component, four-phase system**.

The four phases are :

**(a)** Two solid polymorphic forms :

(i) Rhombic Sulphur ( $S_R$ )

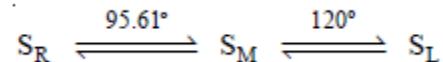
(ii) Monoclinic Sulphur ( $S_M$ )

**(b)** Sulphur Liquid ( $S_L$ )

**(c)** Sulphur Vapour ( $S_V$ )

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

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



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

(i) The six curves *AB, BC, CD, BE, CE, EG*

(ii) The three Triple points *B, C, E*

(iii) The four areas:

*ABG* marked 'solid Rhombic'

*BEC* marked 'solid Monoclinic'

*GECD* marked 'liquid Sulphur'

*ABCD* marked 'Sulphur vapour'

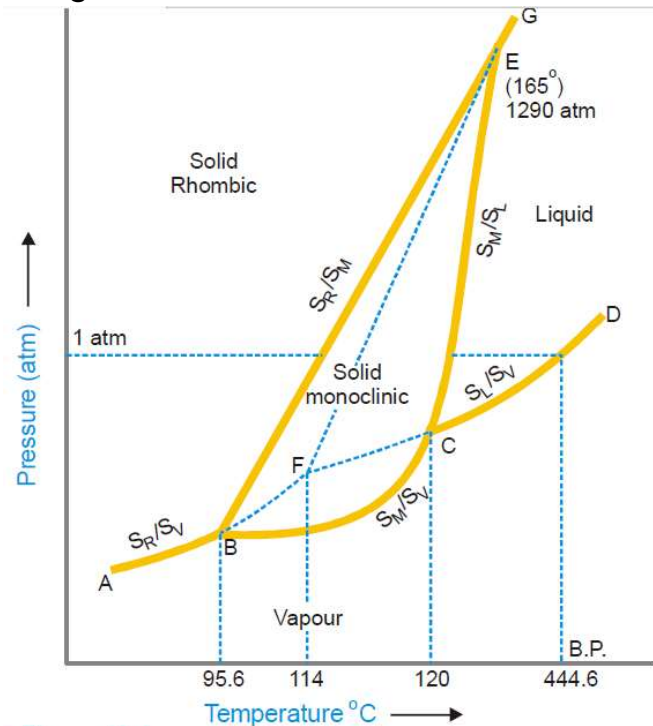
Let us now proceed to discuss the significance of these features :

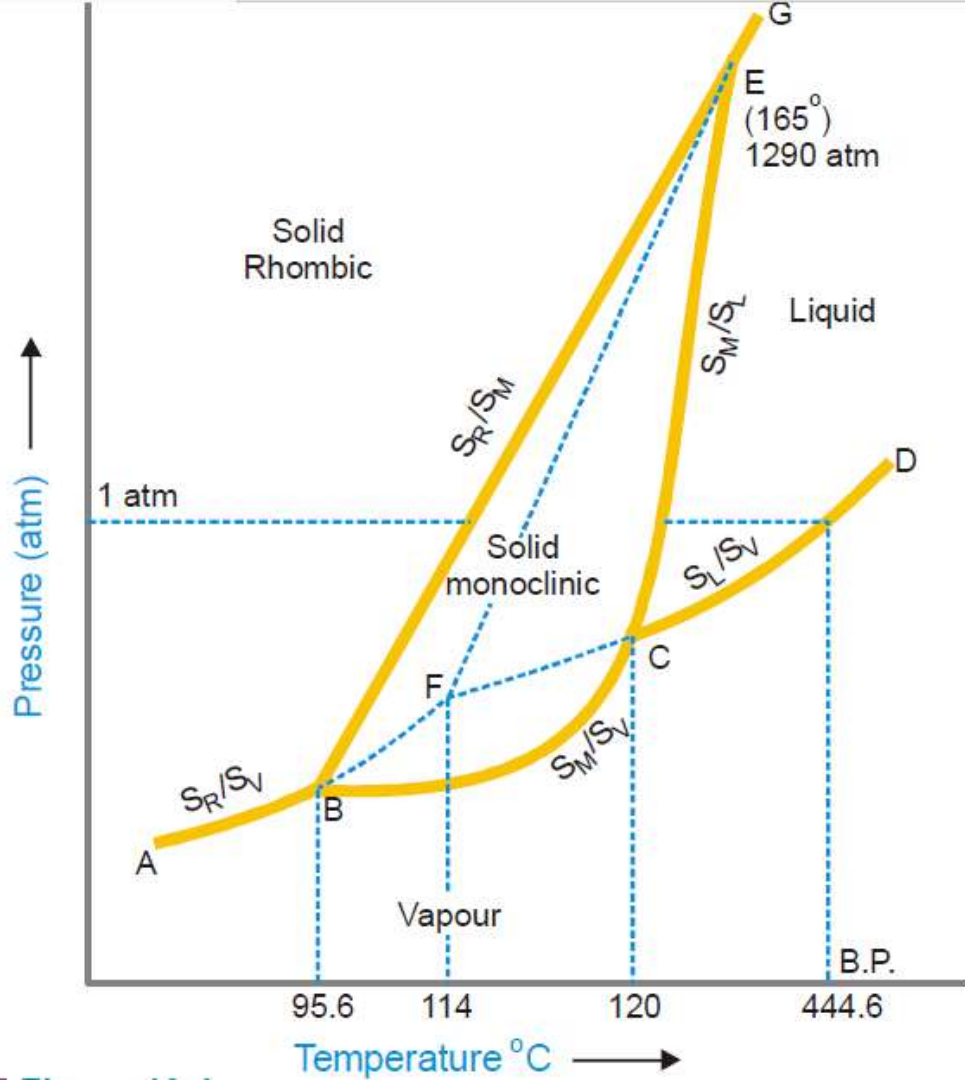
### (1) The curves *AB, BC, CD, BE, CE, EG*

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

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

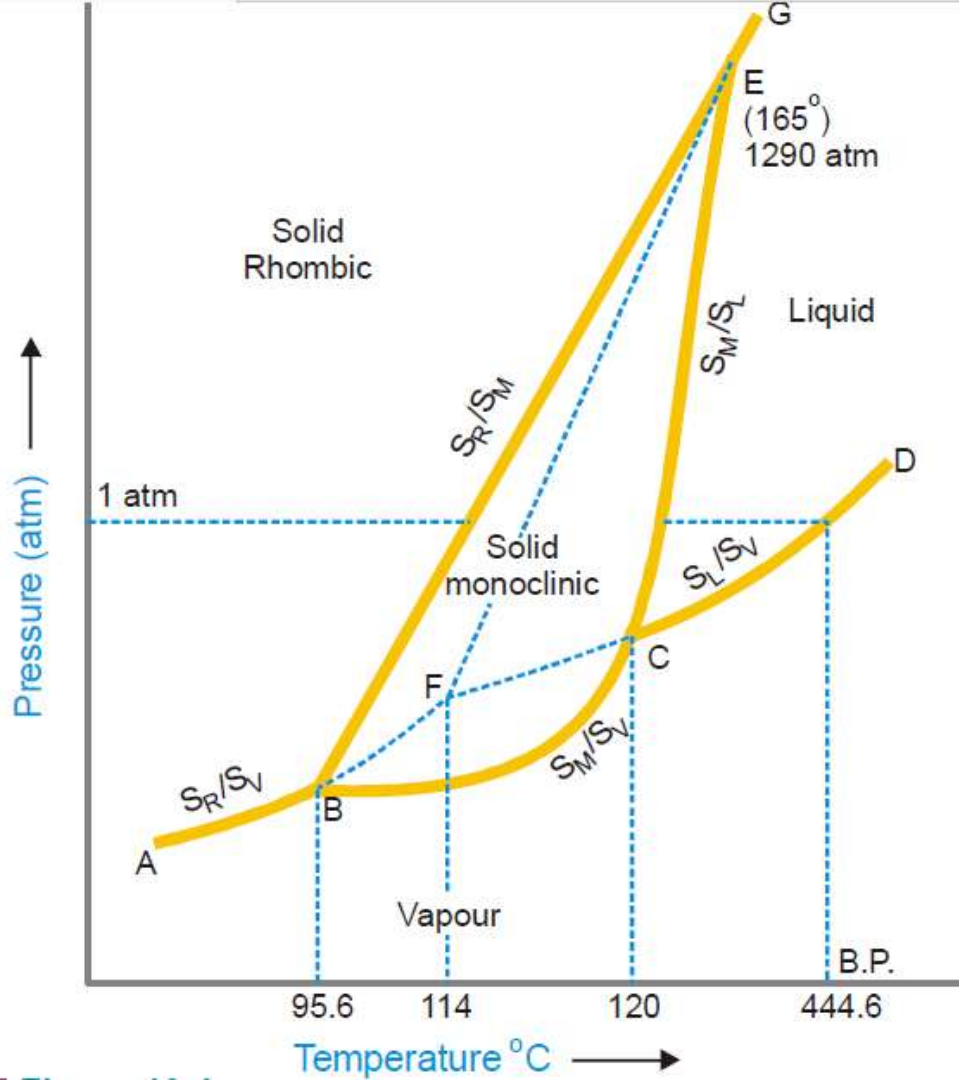
$F = C - P + 2 = 1 - 2 + 2 = 1$  i.e., it is *monovariant*.



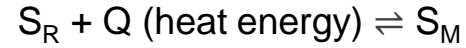


**Curve BC, the Vapour Pressure curve of  $S_M$ .** It shows variation of the vapour pressure of monoclinic sulphur ( $S_M$ ) with temperature.  $S_M$  and  $S_V$  coexist in equilibrium along this curve. The system  $S_M/S_V$  is *monovariant*.

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



**Curve BE, the Transition curve.** It shows the effect of pressure on the transition temperature for  $S_R$  and  $S_M$ . As two solid phases are in equilibrium along the curve, the system  $S_R/S_M$  is *monovariant*.



Thus, with the increase of pressure the transition temperature is raised .

**Curve CE, the Fusion curve of  $S_M$ .** It represents the effect of pressure on the melting point of  $S_M$ . The two phases in equilibrium along this curve are  $S_M$  and  $S_L$ . The system  $S_M/S_L$  is *monovariant*. With a slight increase of volume, the melting point will rise by increase of pressure .

**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

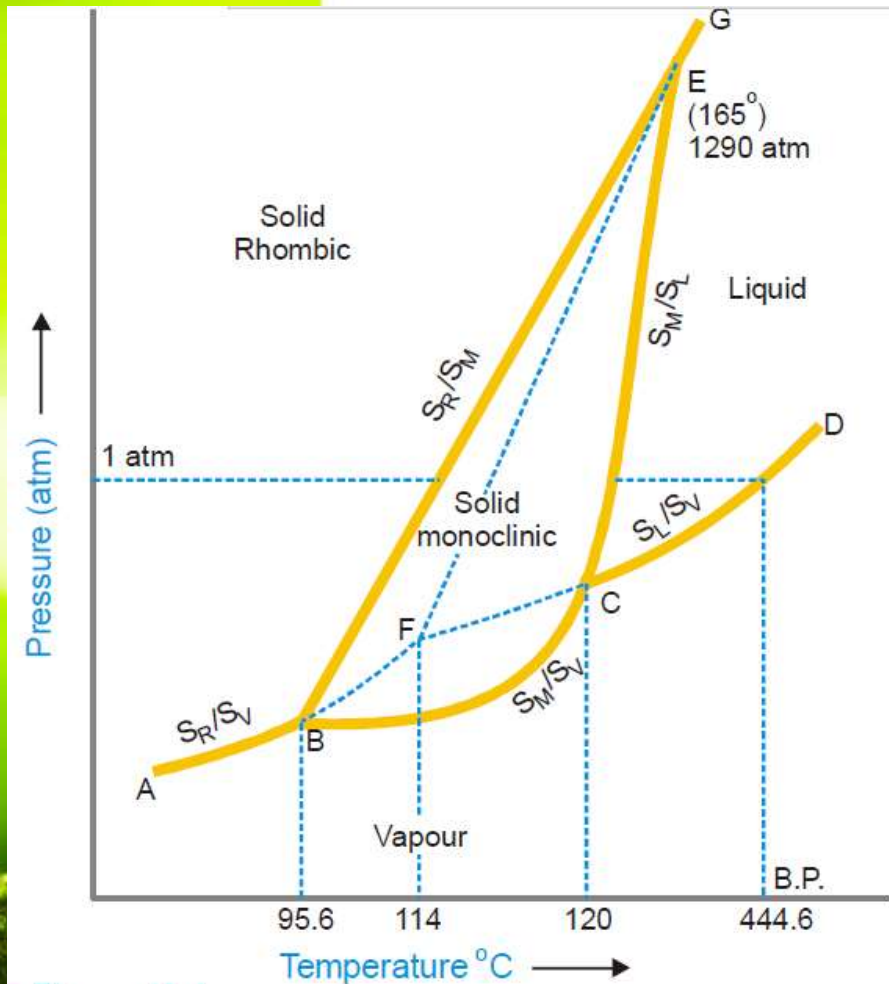
**Triple point B.** This is the meeting point of the three curves AB, BC and BE. Three phases, are in equilibrium at the point B. The system  $S_R/S_M/S_V$  is *nonvariant*.

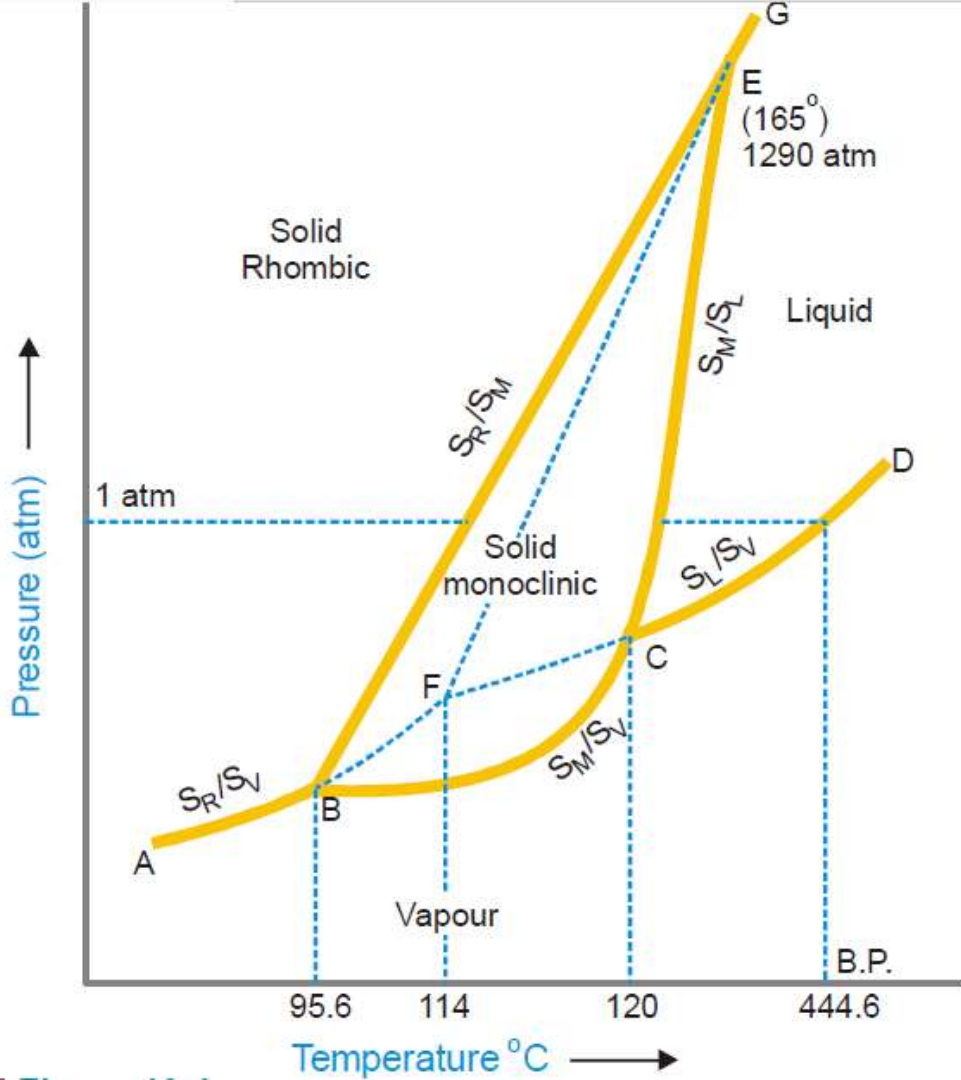
$$F = C - P + 2 = 1 - 3 + 2 = 0$$

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

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

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





### (3) The Areas

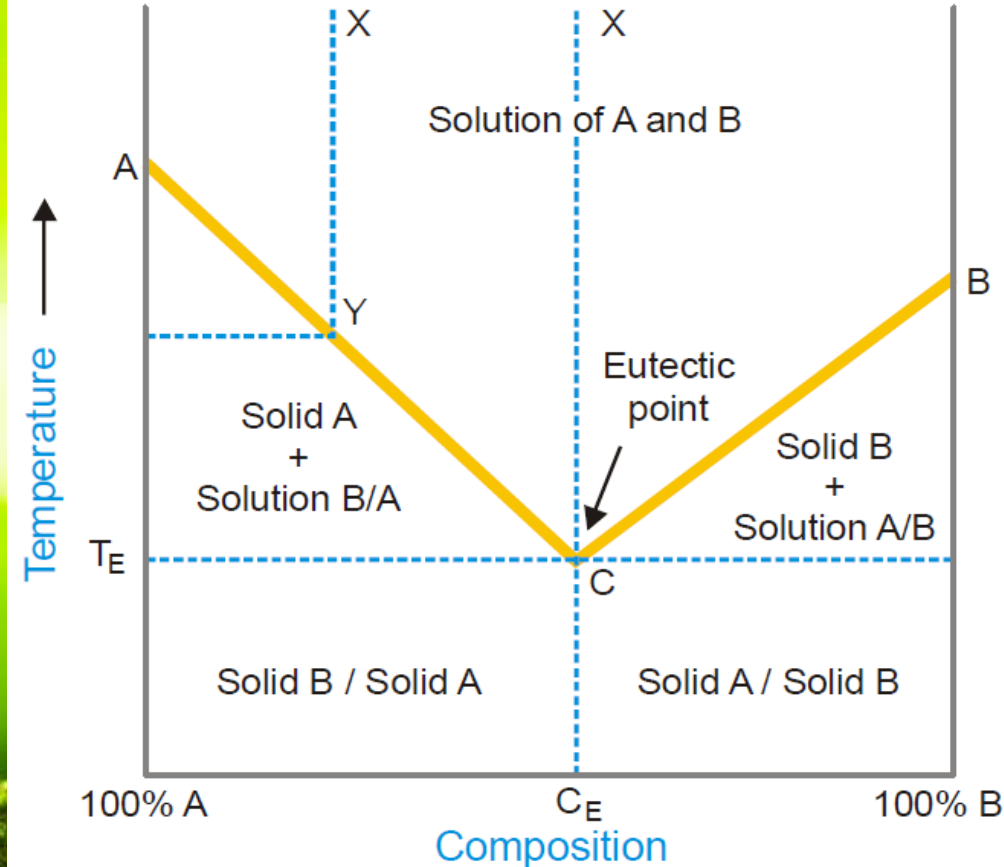
The sulphur system has **four areas** or **regions**. These are rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour.

These represent single phase systems with two degrees of freedom,

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

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

# Two-Component Systems



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

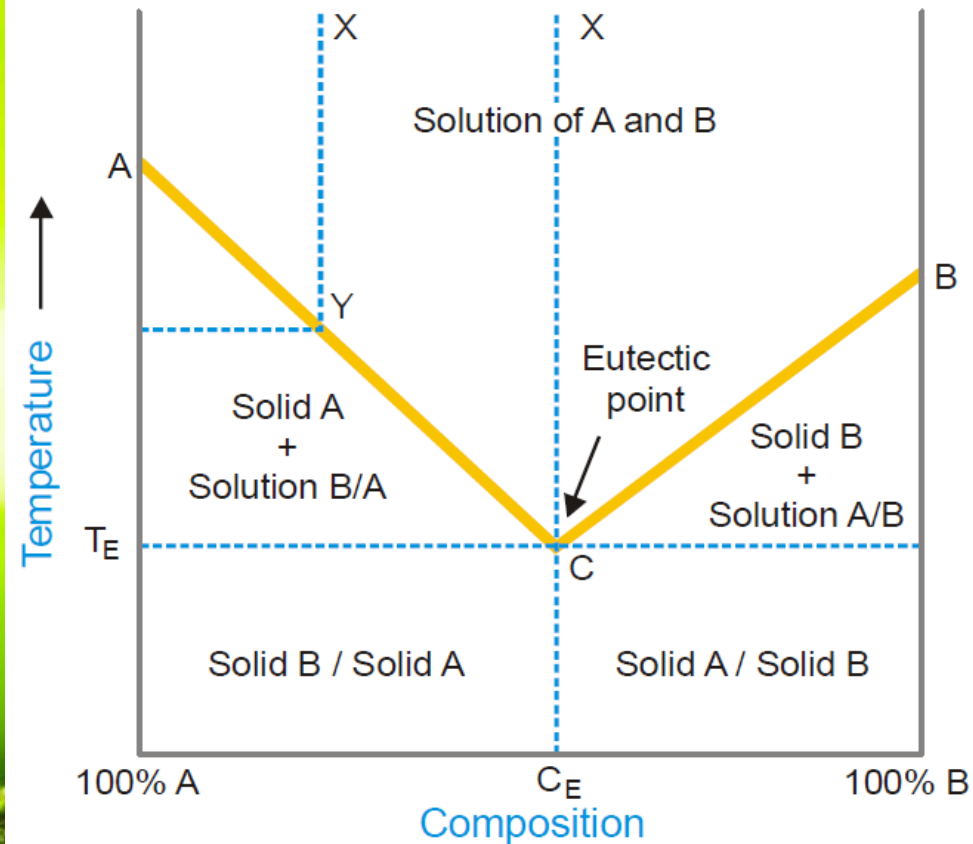
$$F = 2 - 1 + 2 = 3$$

This means that three variables must be specified in order to describe the condition of the phase.

Thus in such a system, in addition to pressure and temperature the concentration of one of the components has also to be given.

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





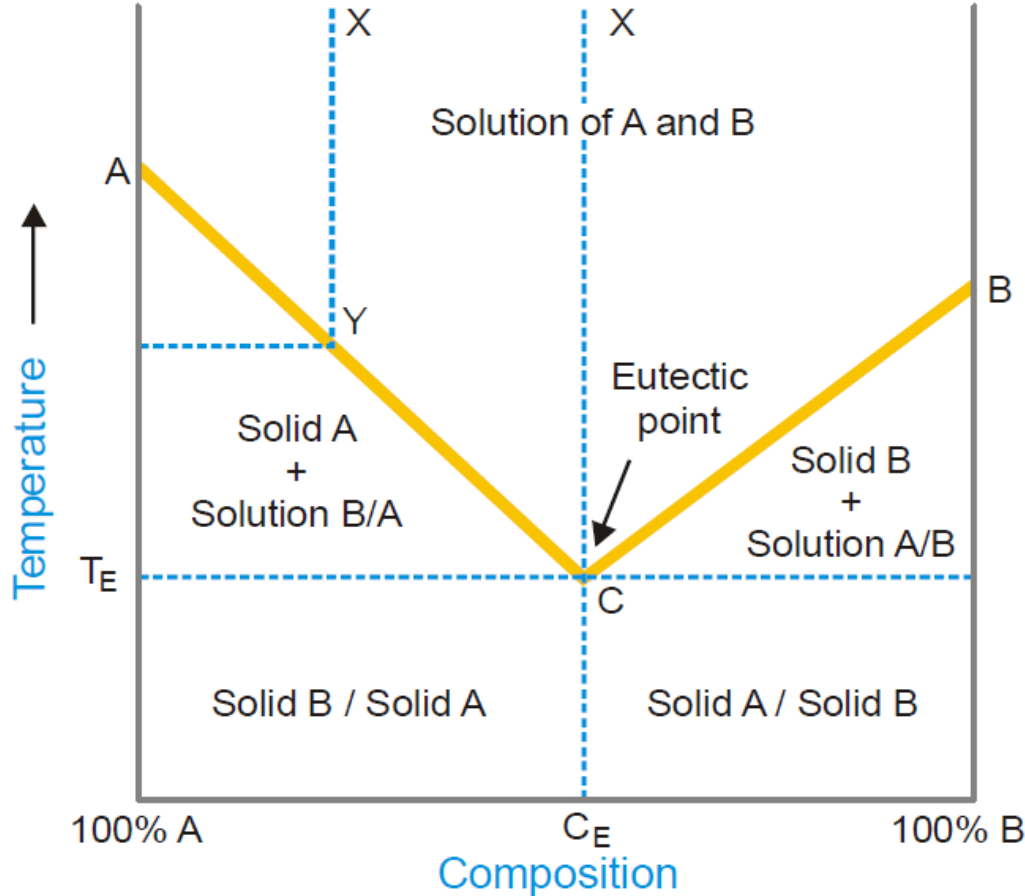
For the sake of having simple plane diagrams we generally consider only two variables, the third one being a constant. For example, for a solid-liquid equilibrium, the gas phase is usually absent and the effect of pressure on the equilibrium is very small.

Thus, when a two-component system consists of solid and liquid phases only, the effect of pressure may be disregarded. Then it is necessary to take into account the remaining variables *viz.*, temperature and concentration.

**Such a solid/liquid system with the gas phase absent is called a condensed system.**

Since the degree of freedom in such a case is reduced by one, we may write the **Reduced Phase rule** as

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

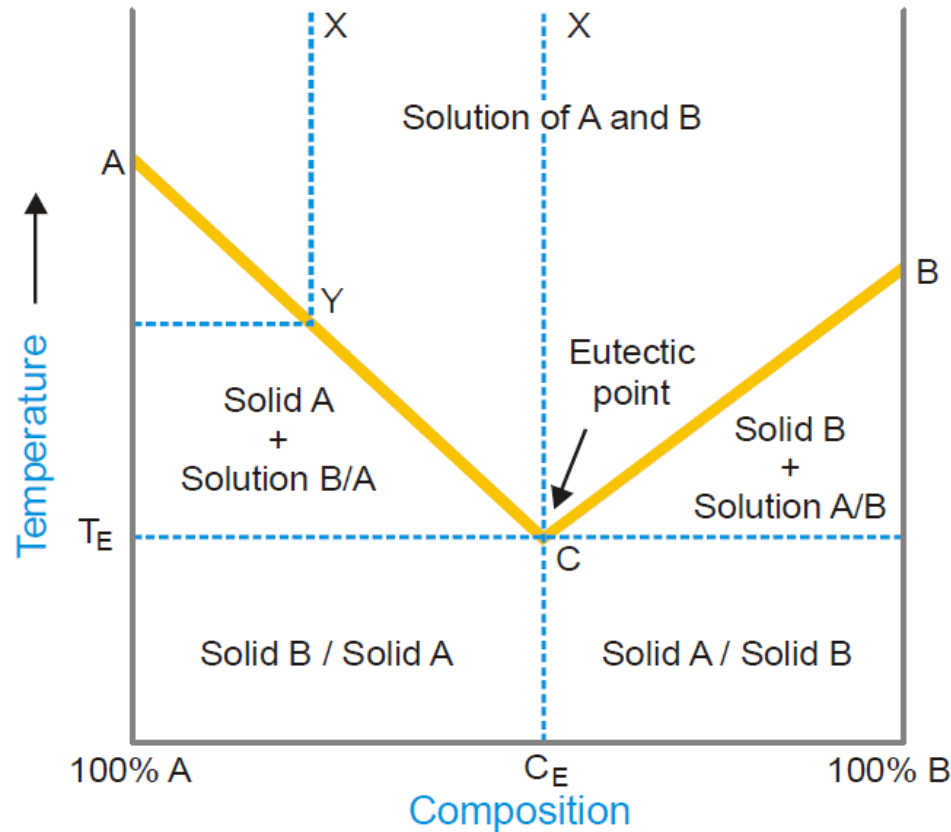


Where,  $F'$  gives the remaining degrees of freedom of the system. The reduced phase rule is more convenient to apply to solid/liquid two-component condensed system. Since the only variables for two-component solid/liquid systems are temperature and composition, the phase diagrams for such systems consist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

## Simple Eutectic Systems

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

## The diagram consists of:



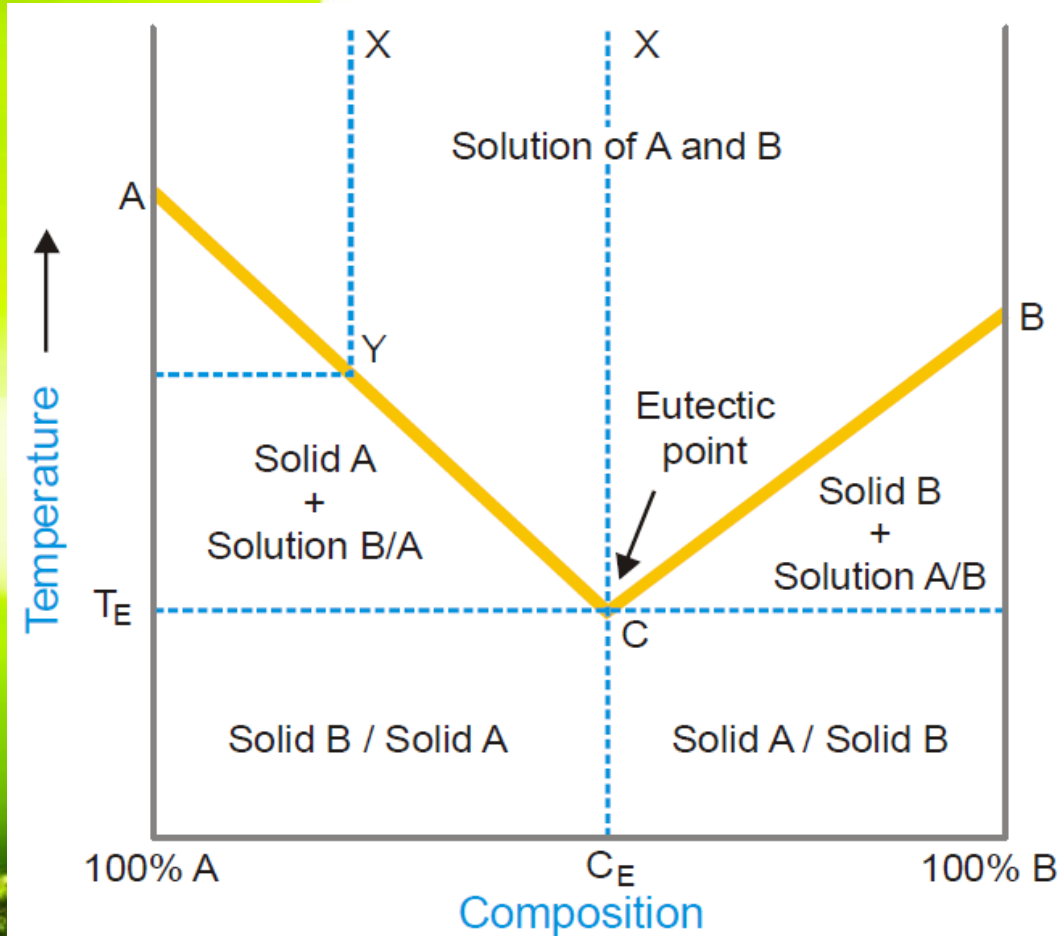
**Curve AC; the Freezing point curve of A.** The point A represents the freezing point of A. The curve AC shows that the freezing point of A falls by the addition of B to A. Thus along this curve, the solid A is in equilibrium with the liquid solution of B in A.

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

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

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

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



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

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

Thus, the system represented by the point C is *nonvariant*. In other words, both temperature and composition of the system solid A-solid B-solution are fixed. The mixture of components A and B as at point C melts at the lowest temperature  $T_E$  indicated on the graph. The *point C* is therefore, called **the Eutectic point** (Greek *eutectos* = easy melting). The corresponding composition ( $C_E$ ) and temperature ( $T_E$ ) are known as the **eutectic composition** and the **eutectic temperature** respectively of the system.

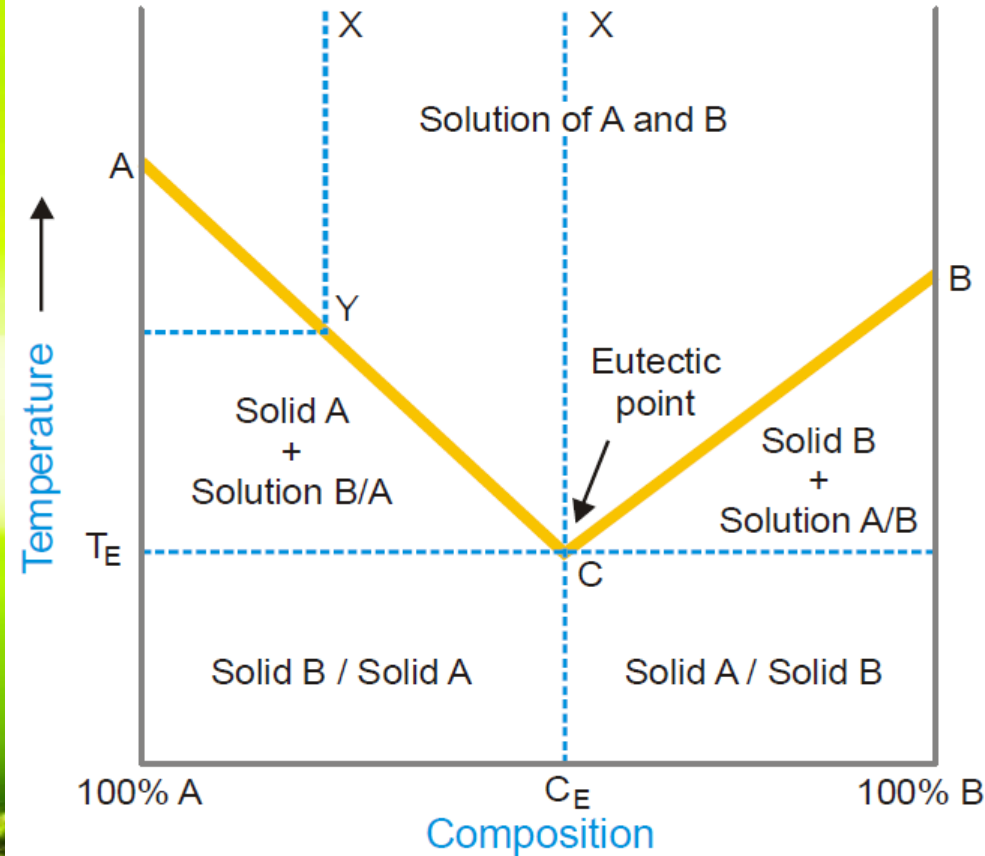
The **eutectic mixture**, although it has a **definite melting point**, is **not to be regarded as a compound**.

The reasons are: **(i)** the components are not in stoichiometric proportions; and **(ii)** on examination under a microscope these reveal the existence of separate crystals of the components.

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

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

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



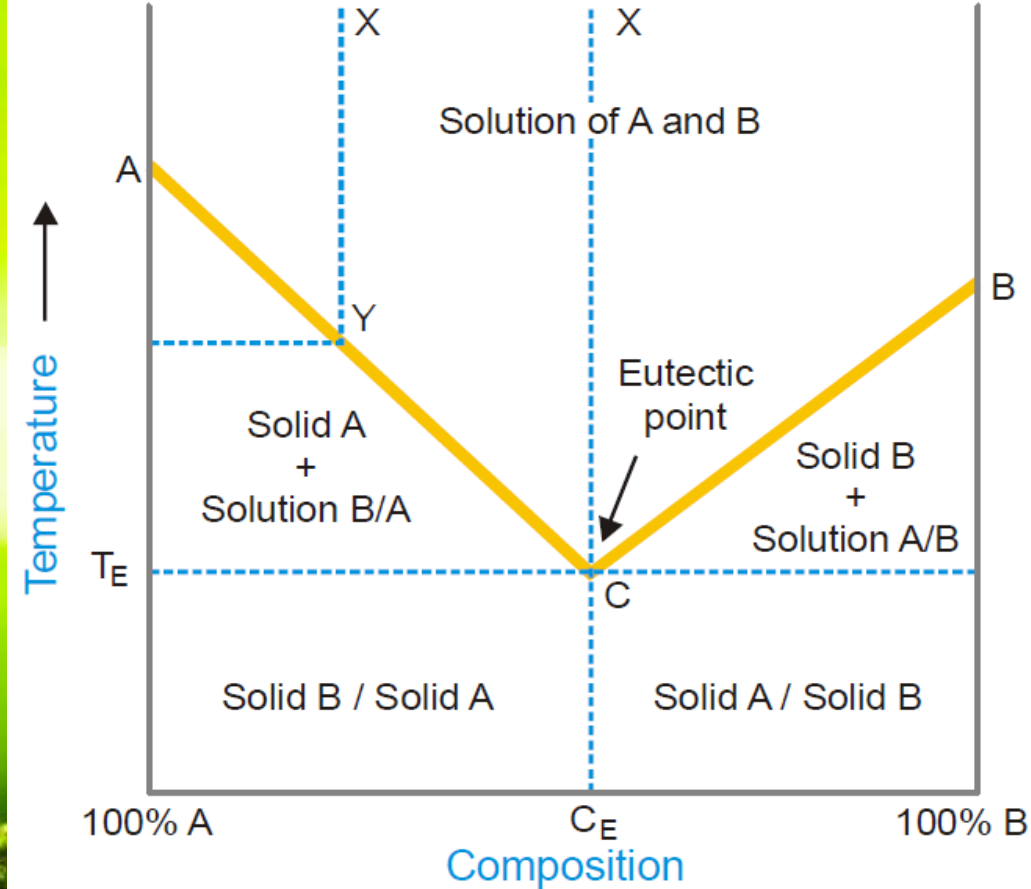
## Effect of Cooling

When the  $A/B$  solution at any point in the area above  $ACB$  is cooled, the cooling dashed line meets the curve  $AC$ , say at  $Y$ . Here solid  $A$  separates and the equilibrium shifts down along the curve  $AC$ . The change of composition and temperature continues till the eutectic point  $C$  is reached when solid  $B$  also separates.

Thus in the area below  $AC$  and above  $T_E$  line, there exist two phases viz., solid  $A$  and solution  $A/B$ , and the system is *bivariant*. Similarly, cooling of solution  $B/A$  on the other side of eutectic, on reaching the curve  $BC$  would yield solid  $B$ /solution system.

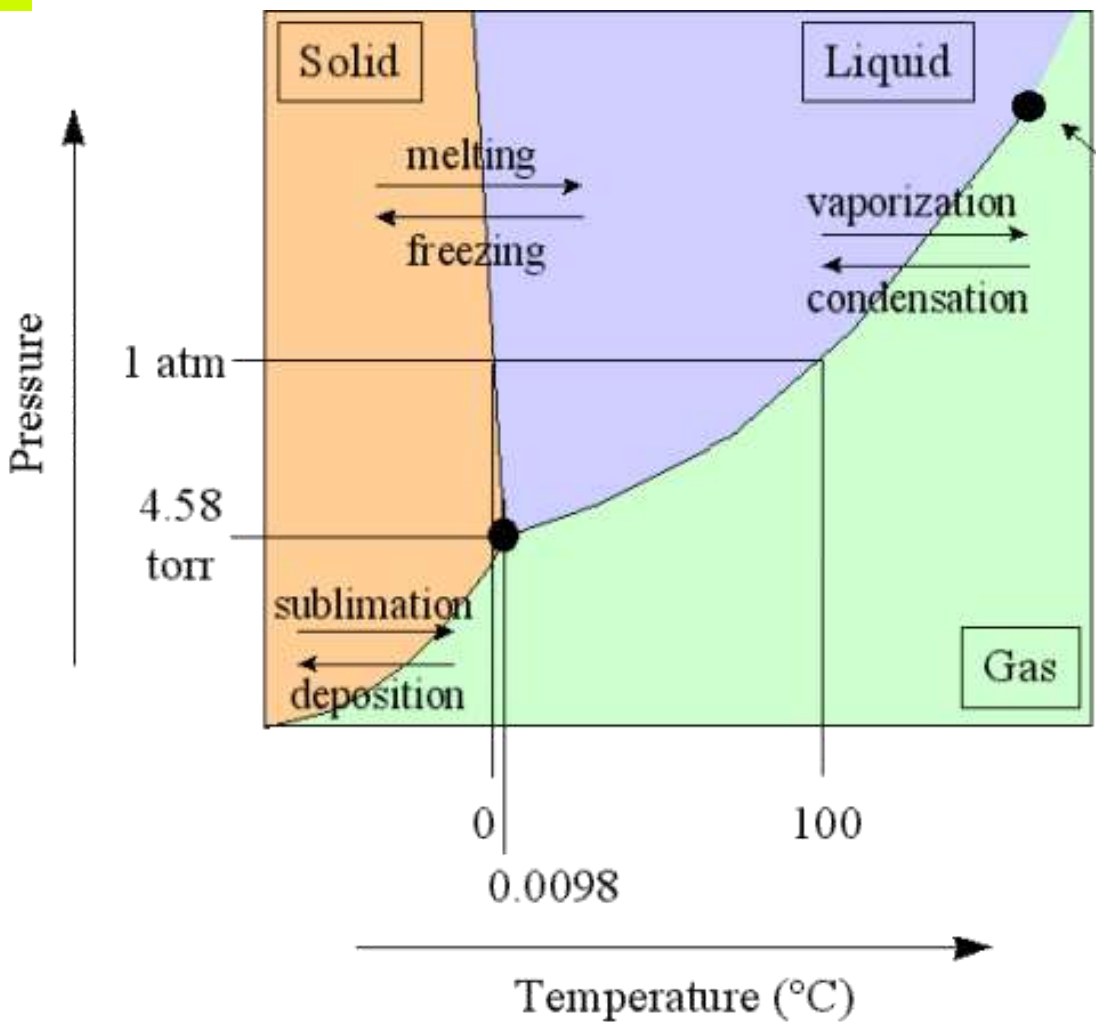
Thus, the area below  $BC$  up to  $T_E$  line would represent solid  $B$  and solution.

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





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# Process

TD 611  
Term Paper

## Pre-treatment

- Method of treating the product prior to freezing Eg. Conc. the product, formulation revision

## Freezing

- Cool the material below its triple point (Complex process)
- Larger crystals are easier to freeze-dry, so slow cooling good (in certain materials)

## Primary Drying

- Lowering of Pressure (to the range of a few millibars)
- Sublimation by supplying heat
- Re-solidification of moisture on Condenser

## Secondary Drying

- Temp. raised to break physico-chemical interactions remove unfrozen water
- Pressure is also lowered in this stage to encourage desorption
- Vacuum is usually broken with an inert gas

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# Freeze Drying



**Solution**

**Temperature  
Time  
Pressure**



**Powder**

# Thermodynamic equilibrium

It is an internal state of a single thermodynamic system, or a relation between several thermodynamic systems connected by more or less permeable or impermeable walls. **In thermodynamic equilibrium there are no net macroscopic flows of matter or of energy, either within a system or between systems.** In a system in its own state of internal thermodynamic equilibrium, no macroscopic change occurs.

**Phase**, in thermodynamics, chemically and physically uniform or homogeneous quantity of matter that can be separated mechanically from a nonhomogeneous mixture and that may consist of a single substance or of a mixture of substances.

Allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner. For example, the allotropes of carbon include diamond (where the carbon atoms are bonded together in a tetrahedral lattice arrangement), graphite (where the carbon atoms are bonded together in sheets of a hexagonal lattice), graphene (single sheets of graphite), and fullerenes (where the carbon atoms are bonded together in spherical, tubular, or ellipsoidal formations).

$$Pv = RT \quad \text{or} \quad PV = nRT$$

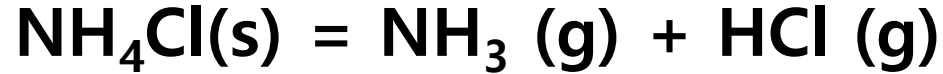
We use the lower case  $v$  to represent the molar volume and the upper case  $V$  to represent the total volume. Thus  $v = V/n$ . This is the ideal gas equation of state.

A eutectic mixture is defined as a mixture of two or more components which usually do not interact to form a new chemical compound but, which at certain ratios, inhibit the crystallization process of one another resulting in a system having a lower melting point than either of the components

**Monoclonal antibodies (mAb or moAb)** are [antibodies](#) that are made by identical [immune cells](#) that are all [clones](#) of a unique parent cell, in contrast to [polyclonal antibodies](#), which are made by several different immune cells.

S No	Drug	T <sub>m</sub> °C	T <sub>m</sub> (Eutectic)°C
1	Allobarbital	173.0	144.0
2	Ergotamine	172.0-174.0	135.0
3	Imipramine HCl	172.0-174.0	109.0

## Dissociation of $\text{NH}_4\text{Cl}$



- Ammonium chloride when heated in a closed vessel dissociates into ammonia and HCl gas. The system consists of two phases solid  $\text{NH}_4\text{Cl}$  and gaseous mixture containing  $\text{NH}_3$  and HCl.
- **However the constituents of the mixture are in the same proportion in which they are combined in solid  $\text{NH}_4\text{Cl}$ .** The composition of the both the phases therefore be expressed in terms of the same chemical individual  $\text{NH}_4\text{Cl}$ . **Thus the dissociation of  $\text{NH}_4\text{Cl}$  is one component system.**