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Phase Rules

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Phase Rules

Phase rule states that "If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the following phase rule equation":

$$F=C-P+2$$

I) Phase (P)

A phase is defined as " an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces".

1. Liquid phase: The number of liquid phase depends on the number of liquids present and their miscibility.

i) If two liquids are immiscible, they will form two separate liquid phases. Example : benzene and water
ii) If two liquids are miscible they will form one liquid phase only. Example : alcohol and water

2. Solid phase Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it. Example : Many forms of sulphur can exist together, but these are all separate phases.

3. Gaseous phase Since a gaseous mixture are thoroughly miscible in all proportions, it will form one phase only. Example : a mixture of N_2 and H_2 forms one phase only.

II) Component (C)

Component is defined as " the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation".

(i) In the water system

$$\text{Ice (s)} \rightleftharpoons \text{Water (l)} \rightleftharpoons \text{Water vapor (g)}$$

The chemical component of all the three phases is H_2O and therefore it is one component system.

(ii) Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus is an one component system.

III) Degree of freedom

Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.

A system having 1,2,3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Consider the water system

Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ Water vapor (g)

The three phases can be in equilibrium only at particular temperature and pressure. Therefore, when all the three phases are present in equilibrium, then no condition need to be specified. The system is therefore zero variant or invariant or has no degree of freedom. In this system if pressure or temperature is altered , three phases will not remain in equilibrium and one of the phases disappears.

Merits of the Phase rule

1. It is applicable to both physical and chemical equilibria.
2. It requires no information regarding molecular/microstructure, since it is applicable to macroscopic systems.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
4. It helps us to predict the behaviour of a system, under different sets of variables.
5. It indicates that different systems with same degree of freedom behave similarly.

6. It helps in deciding whether under a given set of conditions :

a) various substances would exist together in equilibrium (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 can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.

2. It applies only to a single equilibrium system; and provide no information regarding any other possible equilibria in the system.

3. It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus even if a trace of phase is present, it accounts towards the total number of phases.

4. It conditions that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.

5. It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occurs.

Applications of Phase rule to one component system (water system)

The water system is a one component system

Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ Water vapour (g)
(solid) (Liquid) (Gas)

Since water exists in three possible phases such as solid, liquid and vapour, there are three forms of equilibria:

Liquid-vapour , solid-vapour and solid-liquid

Liquid $\rightleftharpoons$ vapour

Solid $\rightleftharpoons$ vapour

Solid $\rightleftharpoons$ Liquid

Each equilibrium involves two phases. The nature of these phases which exist in equilibrium at any time depends on the conditions of temperature and pressure. These conditions have been determined and summarized in the pressure-temperature diagram in which pressure is treated as independent variable and is plotted along y – axis whereas temperature is plotted along x-axis.

The phase diagram for the water system is shown in Figure below

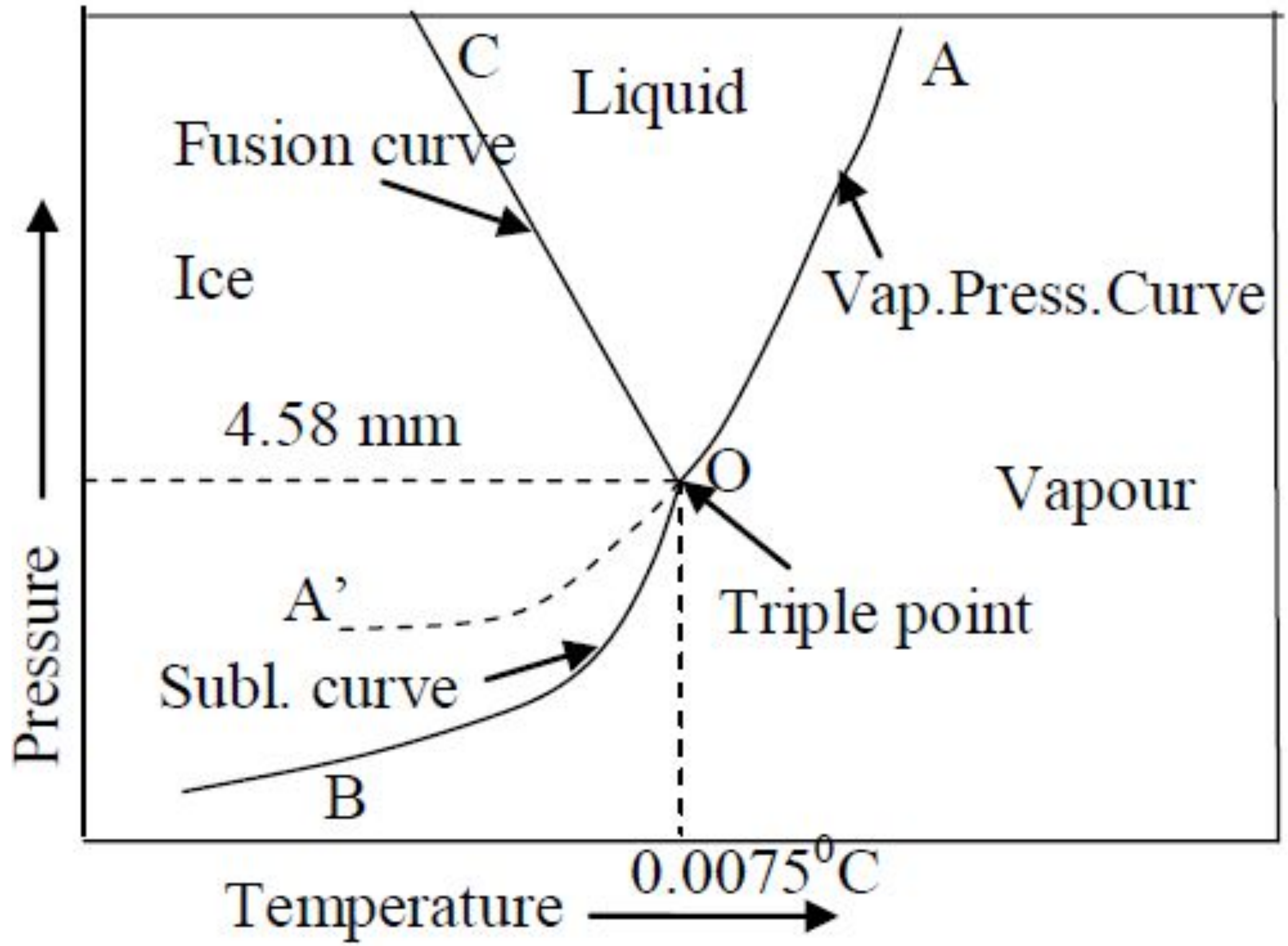

Figure: Phase diagram of water system

The phase diagram consists of following areas

1.Curves : There are three curves OA, OB and OC.

2.Areas : Three curves OA , OB and OC divide the diagram into three areas AOB, AOC and BOC.

3.Triple point : The above three curves meet at the point O and is known as triple point.

4.Metastable equilibrium : The curve OA represents the metastable equilibrium.

1) Curve OA

The curve OA is called **vapourisation curve,** it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.

$$\text{Water} \rightleftharpoons \text{Water vapour}$$

The degree of freedom of the system is one, i.e, univariant. Thus applying phase rule equation,

F = C – P + 2 = 1 – 2 + 2 ; F = 1

This equilibrium (i.e, line OA) will extend upto the critical temperature (3740C). Beyond the critical temperature the equilibrium will disappear only water vapour will exist.

2)Curve OB

The curve OB is called **sublimation curve** of ice, it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

$$\text{Ice} \rightleftharpoons \text{Vapour}$$

The degree of freedom of the system is one, i.e., univariant.

This is predicted by the phase rule.

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

This equilibrium line will extend upto the absolute zero(-273^0C) where no vapour can be present and only ice will exist.

3) Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

$$\text{Ice} \rightleftharpoons \text{Water}$$

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

The degree of freedom of the system is one. i.e., univariant.

iv) Triple point (Point 'O')

At triple point all the three phases namely ice, water and vapour coexist. Thus the value of P is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.00750C and 4.58 mm respectively.

At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases. The triple point is not the same as the ordinary melting point of ice (i.e, 00C). It's value has been increased due to the fact that 00C is the melting point of ice at 760mm of mercury and a decrease of 4.58 mm will rise the melting point to 0.00750C

v)Curve OB (Metastable equilibrium)

The curve OB is called vapour pressure curve of the super-cool water or metastable equilibrium.

Where the following equilibrium will exist.

$$\text{Super-cool water} \rightleftharpoons \text{Vapour}$$

Sometimes water can be cooled below 0^0C without the formation of ice, this water is called super-cooled water. Supercooled water is unstable and it can be converted into solid by 'seeding' or by slight disturbance.

vi) Areas

Area AOC, BOC , AOB represents water ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e., Bivariant.

This is predicted by the phase rule

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