Online Study Material

Course: B. Sc. (Hons./Subs.) Part 2

Subject: Physical Chemistry

Chapter: Phase Equilibrium

Topic: Phase Rule, Definition, One component system-Water system.

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PHASE RULE

Phase Rule was first presented by J. W. Gibbs (1876). Phase Rule is an important tool used for quantitative treatment of system in equilibrium. It enables us to predict the condition that must be specified for a system to exhibit equilibrium. It is also used to calculate the degrees of freedom (F) in the heterogeneous equilibrium system which is not affected by gravity, electrical, magnetic and surface actions.

Statement: 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: **F=C-P+2**

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. The phase rule helps to study the equilibrium in heterogeneous systems and the phase diagram explains the effect of temperature, pressure and concentration on equilibrium.

1. **PHASE (P):** Phase is defined as, "any homogeneous physically distinct and mechanically separable portions of a system which is separated from other parts of the system by definite boundaries". For example:

a) All gases are completely miscible and have no boundaries between them. Hence all gases constitute a single phase.

(b) If two liquids are immiscible, they will form two separate liquid phases. (e.g.) Benzene – Water system. And if two liquids are completely miscible, they will form only one liquid phase. (e.g.) Alcohol - Water system.

(c) Every solid constitutes a separate single phase.

e.g. Decomposition of $CaCO_3$

$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

It involves 3 phases namely solid $CaCO_3$, solid CaO and gaseous CO_2.

2. COMPONENT (C): Component is defined as, "the minimum number of independent variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation". For Example:

(a) Consider a water system consisting of three phases, Ice(s) Water (l) Vapour (g). The chemical composition of all the three phases is H_2O. Hence the number of component is one.

(b) Sulphur exists in 4 phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition is only sulphur. Hence it is a one component system.

(c) Thermal decomposition of $CaCO_3 \rightarrow CaCO_3(s)$ CaO (s) + $CO_2(g)$ The system has 3 phases namely, solid $CaCO_3$, solid CaO and gaseous CO_2 and 2 components, as the composition of each of the above phases can be expressed as equations considering any two of the three components present. When $CaCO_3$ and CaO are considered as components, the chemical equations are:

Phase Components

$CaCO_3 \leftrightarrow CaCO_3 + 0\ CaO$

$CaO \leftrightarrow 0\ CaCO_3 + CaO$

$CO_2 \leftrightarrow CaCO_3 - CaO$

(d) $PCl_5(s) \leftrightarrow PCl_3(l) + Cl_2(g)$ This system has 3 phases and 2 components namely, $PCl_3$and Cl_2.

3. **DEGREE OF FREEDOM (F):** Degree of freedom is defined as, "the minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed in order to define the system completely". A system having 1, 2, 3 or 0 degrees of freedom are called as univariant, bivariant, trivariant and non-variant systems respectively.

APPLICATION OF PHASE RULE FOR ONE COMPONENT WATER SYSTEM

Water can exist in three possible stages, Ice(s), water (l) and vapour (g). All the three phases can be represented by only one chemical constituent H_2O, hence, it is one component system.

For this system C=1; therefore, the formula for degree of freedom of water system will be:

F=C–P+2

If C=1, then F=3-P i.e. for water system degree of freedom depends upon 'P' only. The Phase Diagram of the water system, plotted against pressure and temperature.

Consider the following equilibrium

Ice(s) ↔ Water (l) ↔Vapour (g), Component = 1, Phases = 3

Applying phase rule:

F=1-3+2, F=0

Hence, These 3 phases will be in equilibrium only at a particular temperature and pressure. The system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

Consider the following equilibrium:

Liquid Water(l)↔ Water- vapour (g) or, Ice(s) ↔ Water(l) or Ice(s) ↔Vapour (g)

For any of the above equilibrium, applying phase rule to the above equilibrium,

F = 1-2+2 , F = 1, degrees of freedom is one hence system is univarient/ monovarient i.e.

Therefore the degree of freedom is one.

WATER SYSTEM

Water can exist in three phases, namely, solid, liquid and vapour. Hence, there can be three forms of equilibria, *viz.*,

1. Liquid $\rightleftharpoons$ Vapour 2. Solid $\rightleftharpoons$ Vapour 3. Solid $\rightleftharpoons$ Liquid. Each equilibrium involves two phases. The phase diagram for the water system is shown in Fig. 2.

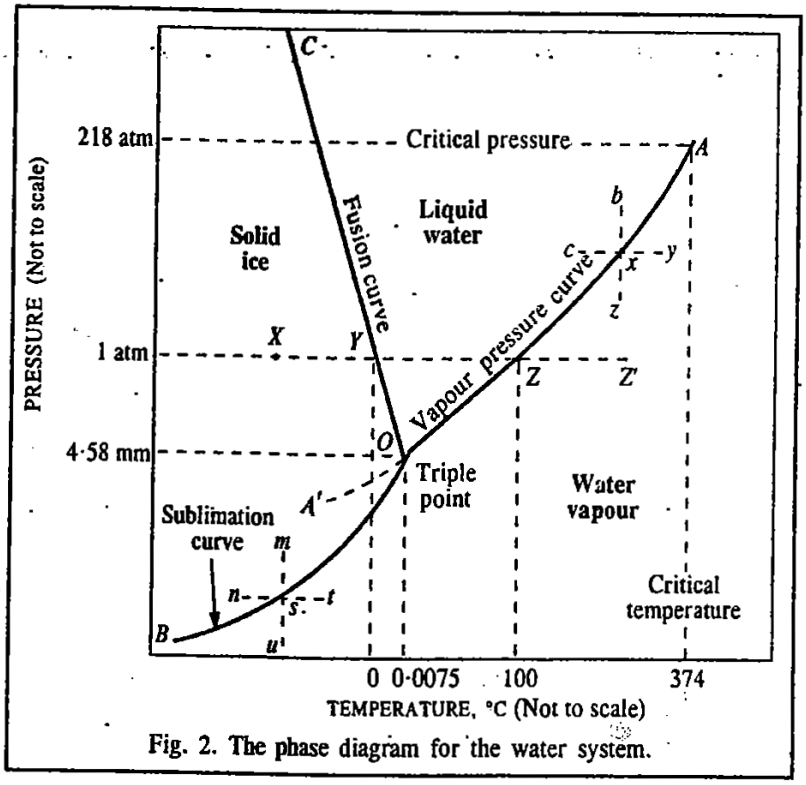

Fig. 2. The phase diagram for the water system.

The curve *OA* represents the equilibrium between liquid water and vapour at different temperatures. It is called the vapour pressure curve of water as it gives the vapour pressure of water at different temperatures. It can be seen that, for any given temperature, there exists one and only one vapour pressure. Similarly, for each vapour pressure, only one temperature can be maintained. Thus, the degree of freedom of the system is one, *i.e.*, the system is univariant :

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

At 100°C, the vapour pressure of water equals the pressure of the atmosphere (1 atm = 760 mm Hg). This is, therefore, the boiling point of water. The curve *OA* extends as far as the critical temperature of water (374°C) since above this temperature liquid water cannot exist.

The variation of vapour pressure with temperature is quantitatively given by Clapeyron equation or Clapeyron–Clausius equation, *viz.*,

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)} \quad \text{or} \quad \ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left\{\frac{T_2 - T_1}{T_1 T_2}\right\}$$

Thank You