MODULE -III

PHASE RULE AND COMPOSITES

3.1 Phase rule

3.2 One Component System (water system}

3.1 Phase rule

The heterogeneous system in equilibrium that is not influenced by gravity or electrical or magnetic forces, but is influenced by pressure, temperature and concentration, then the degree of freedom (F) of the system is related to number of components(C) and number of phases (P) by the phase rule equation,

$$F=C-P+2$$

Uses (or) merits of phase rule

- It is applicable both physical and chemical equilibria.
- It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.
- It helps in deciding whether the given number of substances remains in equilibrium or not.

Limitations of phase rule

- Phase rule can be applied only for systems in equilibrium.
- Only three variables like P, T, & Care considered, but not electrical, magnetic and gravitational forces.
- All the phases of the system must be present under the same conditions of pressure and temperature.
- Solid and liquid phases must not be in finely divided state, otherwise deviations occur.

Phase (P)

Phase is defined as any homogeneous, physically distinct and mechanically separable portion of a system which is separated from other parts of a system by a definite boundary.

Examples

1) Decomposition of $CaCO_3$

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

P= 3

2) Consider water system,

Ice (s) <-> Water (I) <-> Vapour (g)

P= 3.

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.

(eg) Consider water system.,

Ice(s) <-> Water (I) <-> Vapour(g).

Chemical composition of all the three phase is H_2O. So, C = 1

Degree of Freedom

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

If, F = 1 (Univarient system) ,

F = 2 (Bivarient system),

F = 3 (Trivarient system),

Degree of freedom = 0 (Invarient system)

3.2 ONE COMPONENT SYSTEM (WATER SYSTEM}

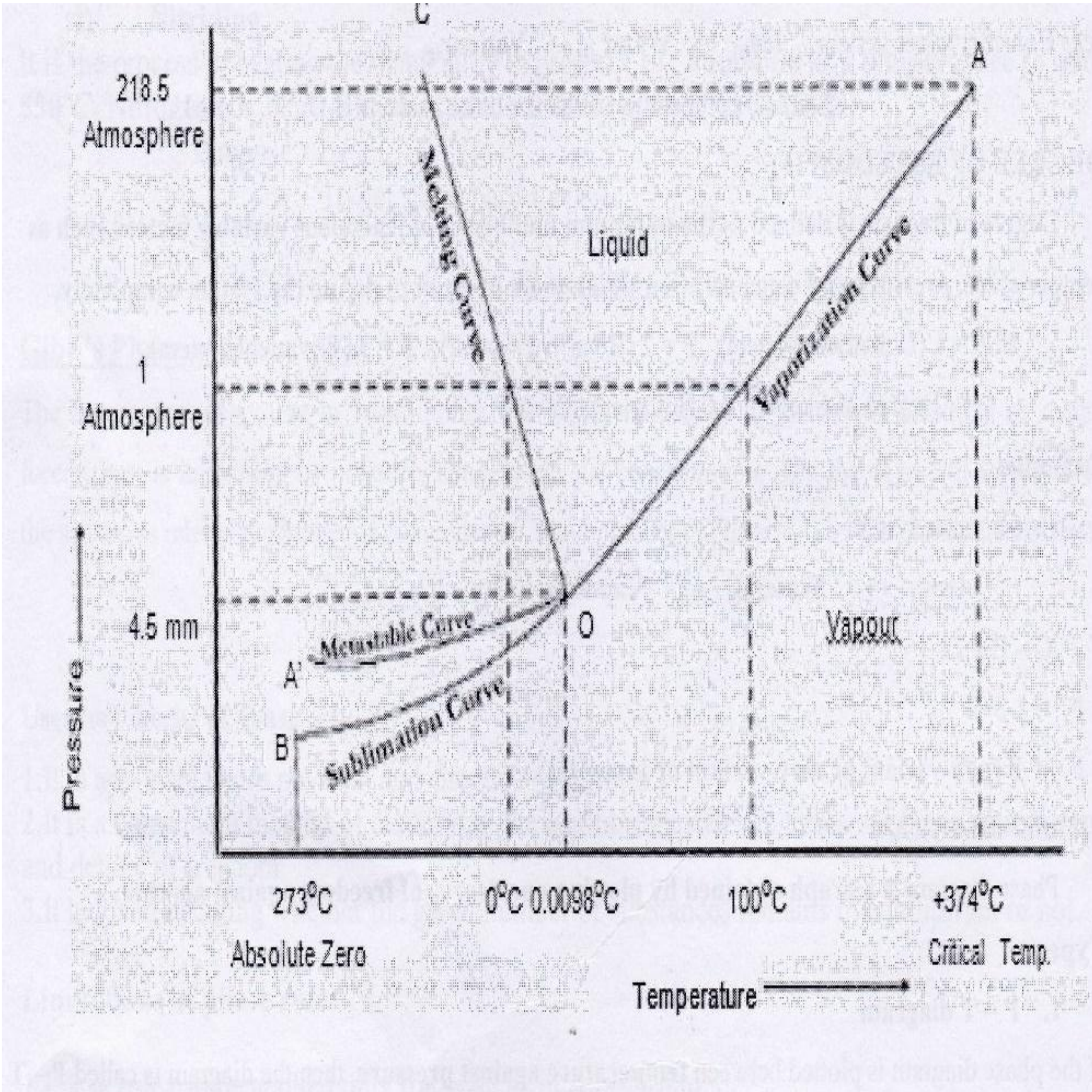
Water exist in three possible phases namely Solid, Liquid and Vapour. Hence there can be three forms of equilibria.

Solid <-> Liquid ,

Liquid <-> Vapour

Vapour <-> Solid

WATER SYSTEM



Source : Engineering chemistry by Dr.Ravikrishnan

Curve OA	Curve OB	Curve OC	Curve OA'
1.)Curve OA is called Vapourisation curve.	Curve OB is called Sublimation curve.	The curve OC is called melting curve.	Curve OA' is called vapour pressure curve of super super cooled water.
2)The equilibrium existing between Water <-> Vapour P =2&C=l	The equilibrium existing between Ice <-> vapour P =2&C=l	The equilibrium existing between Ice <-> water P =2&C=l	The equilibrium existing between super cool water <-> vapour
3)Applying phase rule equation, F = C – P + 2 F=l-2+2 F = 1(univarient)	Applying phase rule equation F = C – P + 2 F=l-2+2 F= 1(univarient)	Applying phase rule equation, F = C- P + 2 F=l-2+2 F=l(univarient)	This equilibrium is called meta stable equilibrium. Super cool water is unstable and it can be converted into solid ice by slight disturbance or seeding.
4)This equilibrium will end up to 374°C. 5)Above this temperature, the equlibrium will disappear, and only vapour will exist.	This equilibrium extend upto-273°C. Above this temperature, vapour cannot be present, only ice exists	The curve OC is slightly inclined towards pressure axis. Above this temperature, liquid exit.	

Areas

Phase diagram has 3 Areas, Area AOC, BOC and AOB

AOC- water,

BOC- ice,

AOB- vapour .

Here P = 2,C = 1

Applying phase rule equation , F = C – P + 2

F=1-1+2

F = 2 (bivarient)

At any point in this area, both temperature and pressure are different. All the three areas are bivarient.

TRIPLE POINT

The curve OA, OB and OC meet at a point "O" called Triple point.

The equilibrium existing is, Ice<-> Water<-> Vapour

P=3 & C=1

Applying phase rule equation,

F = C -P + 2

F=1-3+2

F = 0 (nonvariant)

Temperature and pressure are fixed at this point. (0.0075° C and 4.58 mm)

Conclusion

In water system,

Curves- Univarient
Areas – Bivarient
Point- Invarient