B.Sc. 6th Semester
Physical Chemistry
Section - B
Phase Equilibrium

Phase Diagram of one component System

Water System -

Gibbs Phase Rule

$$F = C - P + 2 \quad - (1)$$

C = no. of components
P = no. of Phases in equilibrium

The least number of phases possible in any system is one. So, according to phase rule equation, a one component system should have a maximum of two degrees of freedom as described below:

$$C = 1, \quad P = 1$$

$$F = C - P + 2$$

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

$$\boxed{F = 2}$$

Hence, one component system requires a maximum of two variables to be fixed to define the system completely.

These two variables are temperature and pressure.

So, phase diagrams of one component systems can be obtained by plotting P v/s T.

Water system is an example of one component system, which is chemically a single compound.

The three possible phases in this system are:

Solid (Ice)

Liquid (water)

Gas (vapour)

The phase diagram of water system is shown in figure-1.

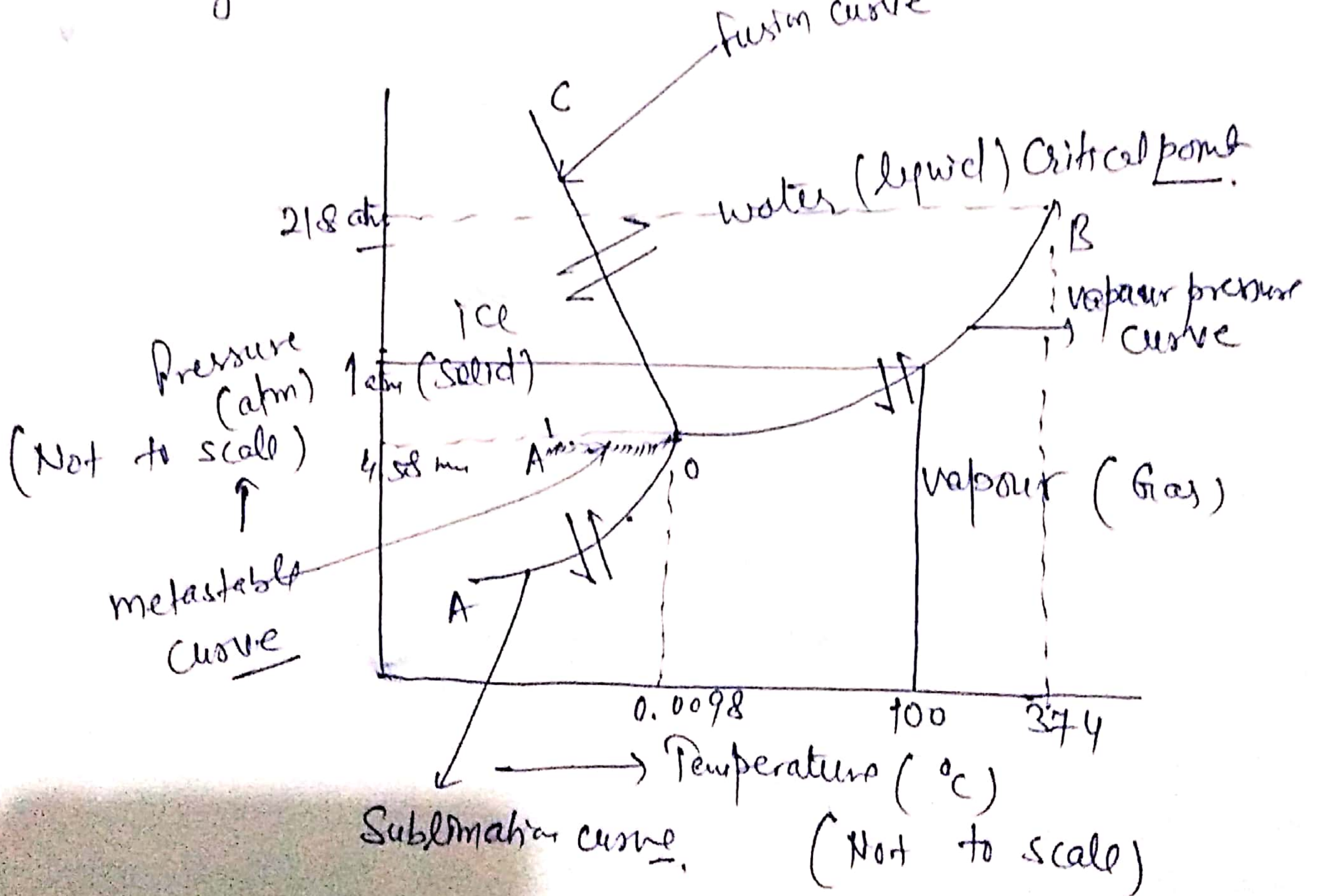

Figure-1 Phase diagram of water system.

Water is three phase system, it can have the following equilibria: (3)

ice $\rightleftharpoons$ vapour

ice $\rightleftharpoons$ water

water $\rightleftharpoons$ vapour

The existence of these equilibria at a particular stage depends upon the conditions of temperature and pressure.

The explanation of phase diagram of water system is as follows:

I Curves. (OA, OB, OC)

a) OA — It is the sublimation curve of ice. Along this curve two phases (ice and vapour) are in equilibrium. Therefore, degree of freedom will be:

$$F = C - P + 2$$
$$= 1 - 2 + 2 = 1 \Rightarrow \boxed{f = 1}$$

Hence, the system is univariant along this curve. It means that only one variable (either temperature or pressure) is sufficient to be fixed in order to define the system.

b) OB and OC — Similarly as in case of OA, along OB and OC two phases are in equilibrium. Therefore, in these cases also, system is univariant.

The curve OB is known as vapour pressure curve of water. With rise in temperature, the vapour pressure increases.
We can use the curve OB to decide how the boiling temperature varies with changing external pressure.
For example, at an altitude of 12 km, when the external pressure is 19.9 kPa, water boils at 60 °C because that is the temperature at which the vapour pressure is 19.9 kPa.

{Important}
The slope of curve OC is negative, which means that ice melts with decrease in volume. It implies as the pressure is raised, the melting temperature of ice falls.
Ice has a very open crystal structure in which the water molecules are held apart by the hydrogen bonds between them. This open cage structure collapses on melting and the liquid is denser than the solid.

(c) Metastable curve OA'

The curve OA' is a continuation of curve BO. The curve OA' represents water (l) and water (vapour) in metastable equilibrium. It is sometimes possible to cool liquid water below the point O without solidification as shown by dotted curve OA'. The liquid below the freezing point is in super cooled state which is not quite stable and is known as metastable water.

(d) The Point 'O' (Triple Point)

At this point three phases (solid, liquid and gas) are in equilibrium. The degree of freedom

$f = C - P + 2$

$= 1 - 3 + 2 = 0$ $\boxed{f = 0}$

The system is invariant at this point.

If either the temperature or pressure or both are changed, the three phases would no longer co-exist and at least one of them would disappear.

(e) Areas. AOB, BOC, AOC

Area	Phase (P)	Degree of freedom ($f = C - P + 2$)
AOB	vapour (1)	$f = 1 - 1 + 2 = 2$
BOC	water (1)	$f = 1 - 1 + 2 = 2$
AOC	Ice (1)	$f = 1 - 1 + 2 = 2$

Hence, each area is a bivariant system. So, it becomes necessary to specify both the temperature and pressure to define a one phase system.

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