Phase Diagram
of
Water System

Phase Rule

Willard Gibbs proposed Phase Rule, which explains the equilibrium existing in heterogeneous systems.
It states that the equilibrium between different **phases** is influenced by temperature, pressure and concentration only and not by gravity, electrical or magnetic forces.

According to this rule, "In a heterogeneous system in equilibrium, the number of degree of freedom plus the number of phases is equal to the number of components plus two."

Mathematically,
F+P=C+2
or **F=C-P+2**

Where,
F=No. of degree of freedom
C=Number of components
P=Number of Phases
2=Additional variables of temperature and pressure

Phase

The physically distinct, homogenous and mechanically separable parts of heterogeneous system are called as Phases.

Examples

1. A gaseous mixture : A single phase system because gases are completely miscible
2. Mixture of miscible liquids like (Water+Alcohol), (Benzene+Chloroform) etc
3. A liquid consisting of vapors in equilibrium is a two phase system
4. Mixture of immiscible liquids like (CCl_4 + H_2O) is a two phase system
5. Ice – Liquid water – Water Vapor - system is a three phase system
6. Alloys are solid homogenous solution so they are single phase system
7. $CaCO_3 \rightarrow CaO + CO_2$ is a three phase system

Components

The minimum number of independently variable constituents which are required to express the components of each phase in the system, is called as components.

Examples

Ice $\rightarrow$ Water $\rightarrow$ Vapor
Solid $\rightarrow$ Liquid $\rightarrow$ Gas
H_2O H_2O H_2O
The chemical compound of the three phases is H_2O, So, it is a one component system

Degree of Freedom

The minimum number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely is called as Degree of Freedom.

If, F = 0, (Invariant)

F = 1, Univarient or Monovariant

F= 2, Bivariant

F = 3, Trivariant

Phase Diagram

A phase diagram is the description of the behavior of the phases under equilibrium.
i.e. the number of phases that exists at equilibrium depends upon the condition of temperature & pressure or Temperature & composition (Pressure remains constant).

So, The phase diagram describes the condition in which various phases will constitute the system that is a graph between Pressure and Temperature.

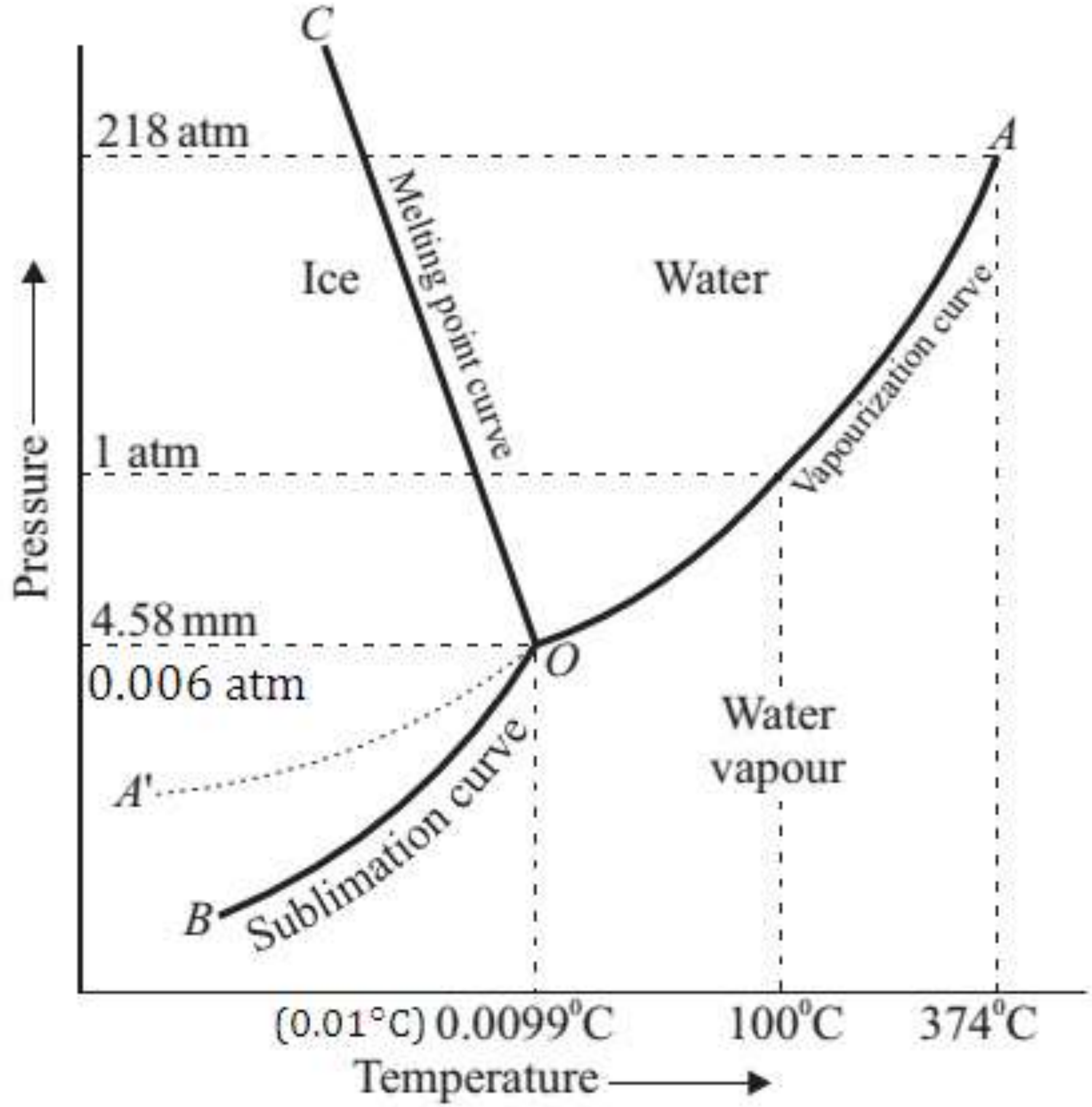

Fig. Phase diagram for the water system

Water System

Water exists as Ice (solid), Water (liquid) and Vapors (gas) in following possible equilibrium.

Ice (Solid) $\rightleftharpoons$ water (Liquid)

Water (Liquid) $\rightleftharpoons$ Vapour (Gas)

Ice (Solid) $\rightleftharpoons$ Vapour (Gas)

Ice (Solid) $\rightleftharpoons$ Water (Liquid) $\rightleftharpoons$ Vapor (Gas)

Maximum, Number of Phases possible when,

$F = 0$

$F = C - P + 2$

Thus,

$P = C - F + 2$

$P_{max} = C + 2$

For,

One component system, $C = 1$, Then $P_{max} = 3$

Two component system, $C = 2$, Then $P_{max} = 4$

Three component system, $C = 3$, Then $P_{max} = 5$

Significance of Variance (Degree of Freedom)

- **If, F = 0, Invariant or Non-variant**:The system does not exist if either of the temperature, pressure or concentration is changed
- **If, F = 1, Univariant or Monovariant:** Any one variable of temperature, pressure or concentration can be changed.
- **If, F = 2, Bivariant:** any two variables of temperature, pressure or concentration can be changed.
- **If, F = 3, Trivariant:** All the three variables temperature, pressure and concentration can be changed.

Phase Diagram of water

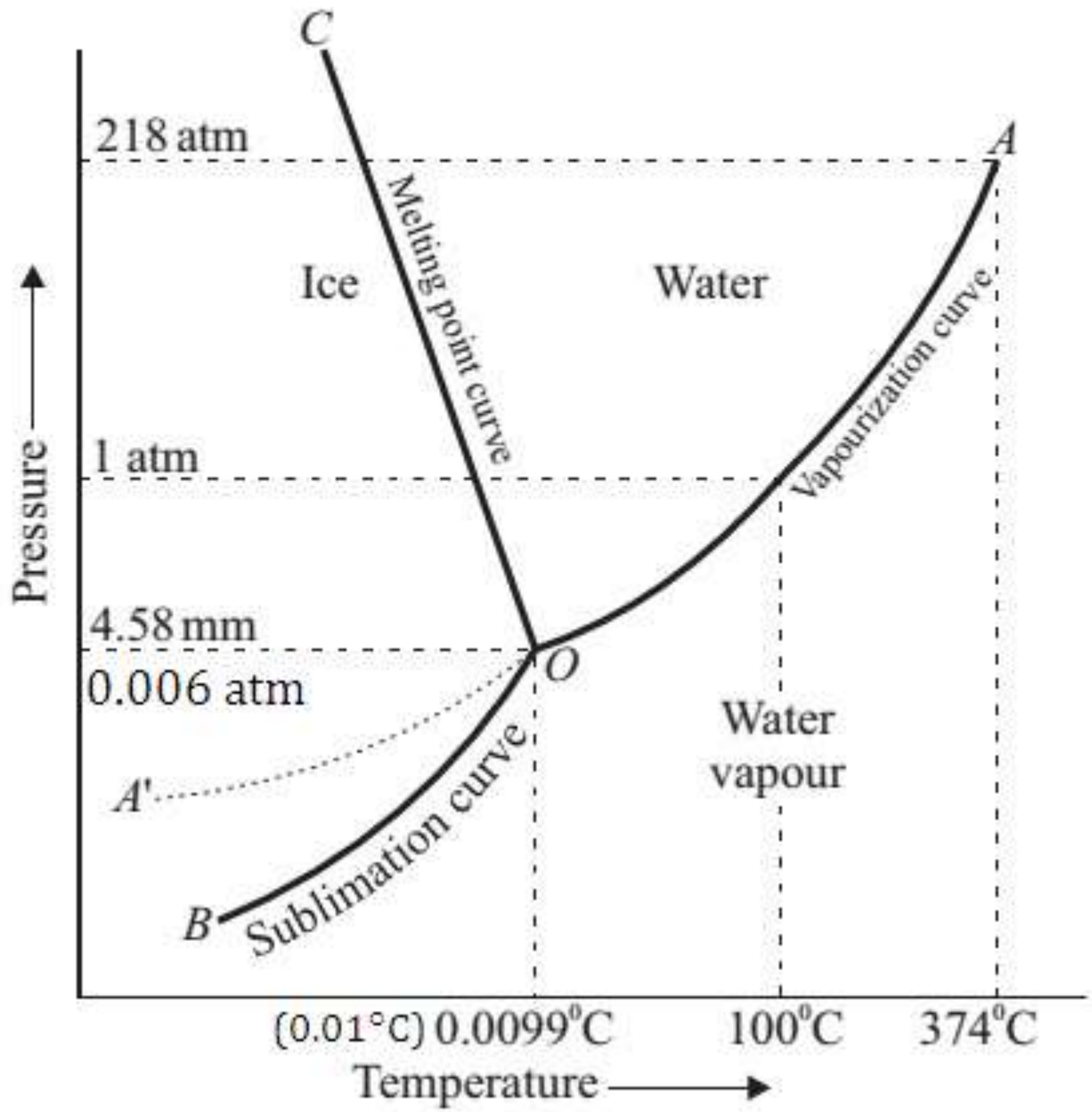

Fig. Phase diagram for the water system

The phase diagram consists of

1. Stable Curves – Three Curves

i. **OA** Vaporization Curve (Liquid – Gas eqm.)

ii. **OB** Sublimation Curve (Solid – Gas eqm.)

iii. **OC** Melting (Fusion) Curve (Solid – Liquid eqm.)

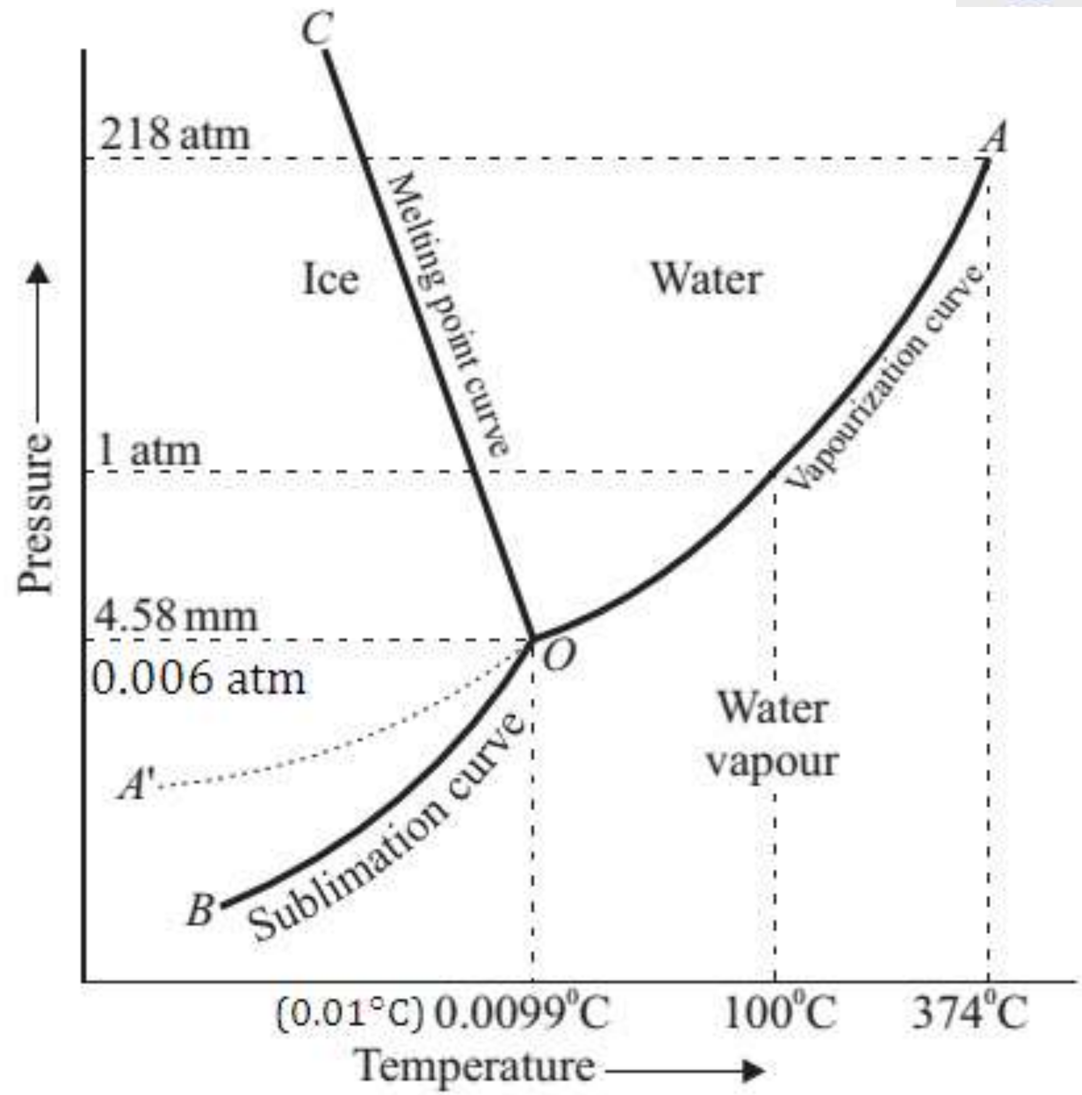

Fig. Phase diagram for the water system

2. Meta Stable Curve – One Curve OA’

3. Areas –

Three areas

i. Area Δ AOB –

Water Vapour

ii. Area Δ COB –

Solid (Ice)

iii. Area Δ AOC –

Liquid water

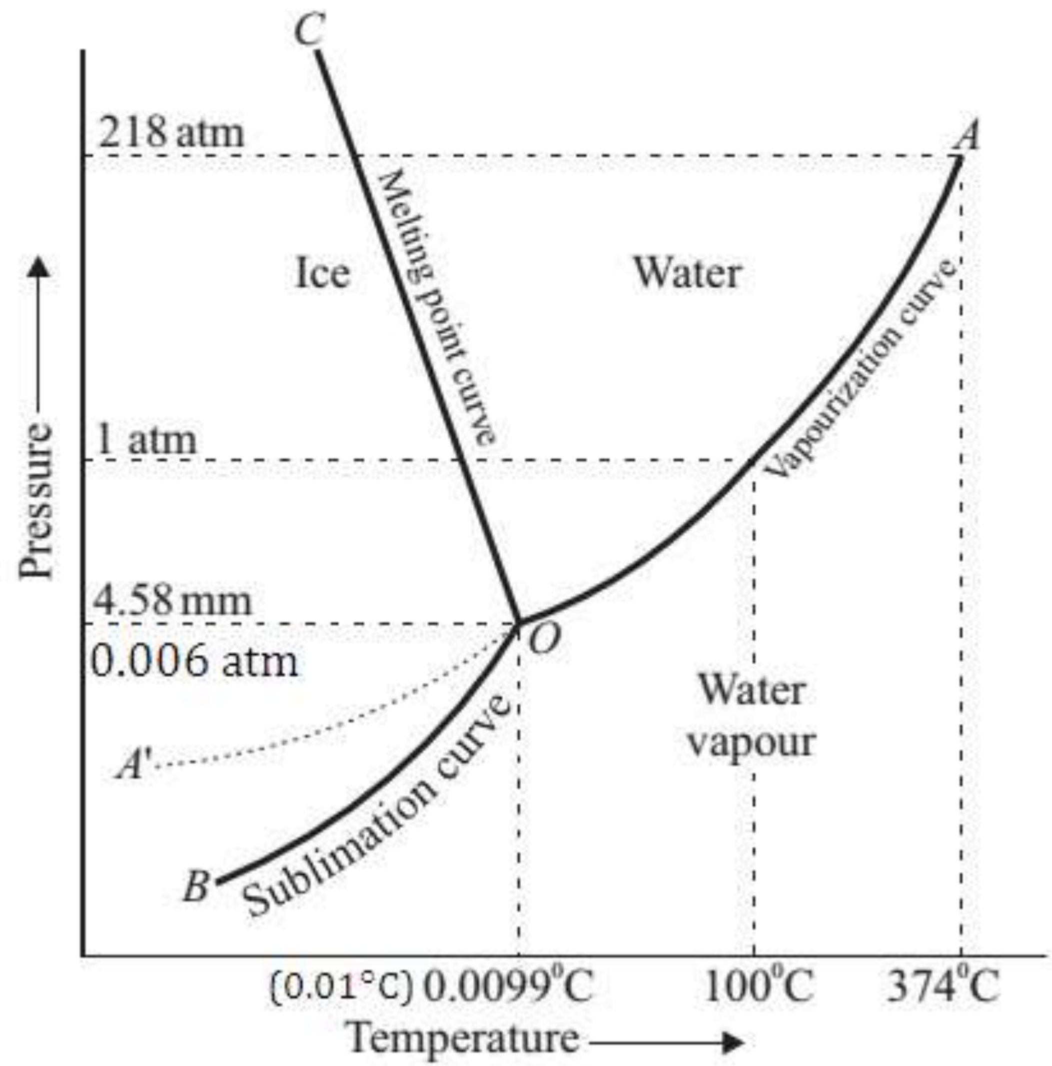

Fig. Phase diagram for the water system

4. **Triple Point – One 'O'**
   All the three states (Solid, Liquid,Gas) co-exist or exist together at this point.

5. **Critical Point:**
   The maximum temperature and pressure **above which water cannot exist.**

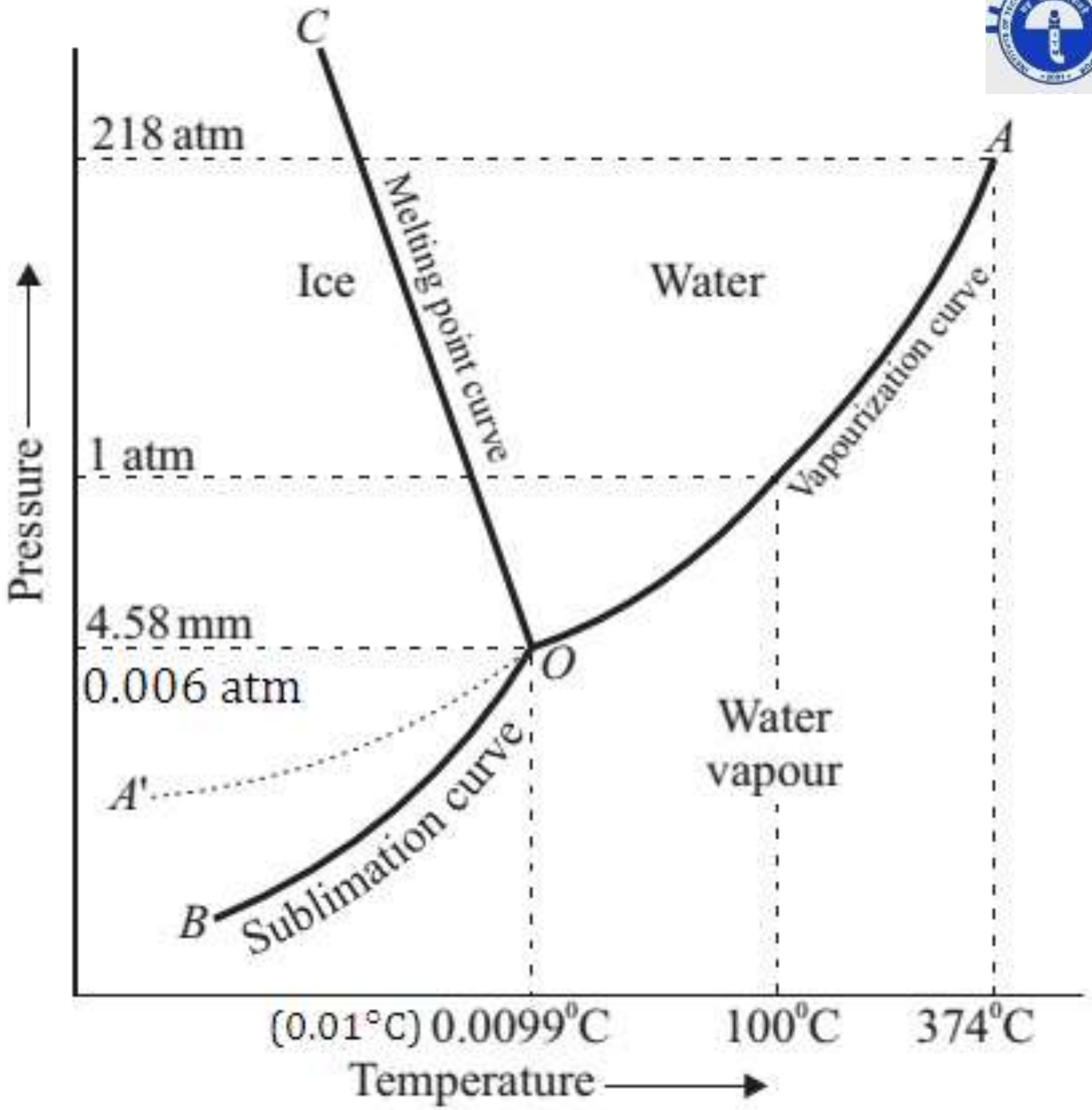

Fig. Phase diagram for the water system

Explanation

1. Curves

i. Sublimation Curve (OB)

Solid (Ice) – Gas (vapor) Equilibrium

At the curve line (Boundary) two phases are in equilibrium

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

$= 1 - 2 + 2$

= 1(Univariant)

ii. Vapor Pressure Curve (OA)

Liquid – Gas (vapor) Equilibrium

At the curve line (Boundary) two phases are in equilibrium

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

$= 1 - 2 + 2$

= 1(Univariant)

iii. Fusion Curve (OC)

Solid (Ice) – Liquid Equilibrium

At the curve line (Boundary) two phases are in equilibrium

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

$= 1 - 2 + 2$

= 1(Univariant)

2. Meta Stable Curve (OA')

Curve OA' is in continuation with curve "AO" when water is super cooled below its freezing point.

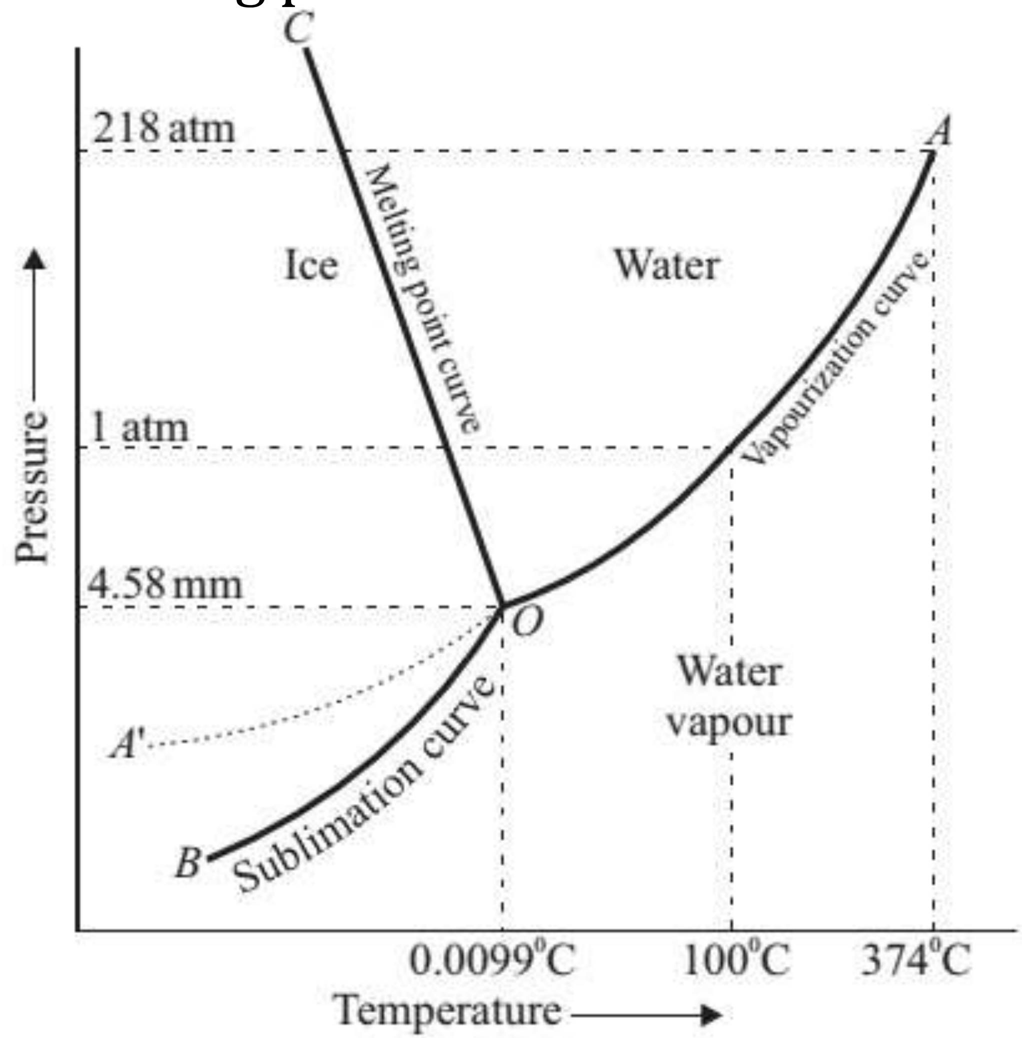

Fig. Phase diagram for the water system

3. Areas

i. Area Δ AOB Vapor Phase: Only one phase

$$P = 1, C = 1, \text{So, } F = C - P + 2$$
$$= 1 - 1 + 2$$
$$= 2 \text{(Bivariant)}$$

ii. Area Δ AOC Liquid Phase: Only one phase

$$P = 1, C = 1, \text{So, } F = C - P + 2$$
$$= 1 - 1 + 2$$
$$= 2 \text{(Bivariant)}$$

iii. Area Δ COB Solid Phase: Only one phase

$$P = 1, C = 1, \text{So, } F = C - P + 2$$
$$= 1 - 1 + 2$$
$$= 2 \text{(Bivariant)}$$

4. Triple Point

The point at which all the three phases of the water (ice (solid), liquid, gas (Vapor)) co-exist. At temperature 0.0099 °C (~0.01°C) and pressure 0.006 atm (4.58 mm Hg). the Triple Point exists.

At this point,

$$C = 1, P = 3, \text{So, } F = C - P + 2$$
$$= 1 - 3 + 2$$
$$= 0 \text{ (Invariant)}$$

Thus, If any of the condition temperature or pressure is changed the Triple Point will not exist anymore.

5. Critical Point

In thermodynamics, a Critical Point is the 'End Point'. In water system Critical Temperature is 374°C and Critical Pressure is 218 atm. Above these points water cannot exist in any phase.

Thank You

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