



ENGINEERING CHEMISTRY

Department of Science and Humanities

ENGINEERING CHEMISTRY

Module 2- Phase equilibria



Class content:

- *Phase diagram of a 1-component system*
- *Phase diagram of water*

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Phase diagram

A diagram which represents the **conditions** under which a substance exists in **different phases** in a system

Phase diagram of a 1-component system

$$F = C - P + 2$$

For a 1-component system $F = 3 - P$

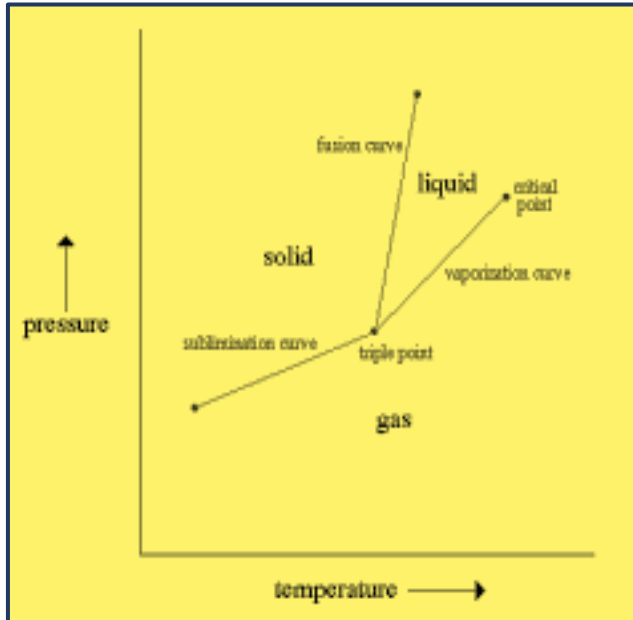
Single phase : $F = 2$; Area in a diagram

Two phases in equilibrium : $F = 1$; line in a diagram

Three phases in equilibrium : $F = 0$; point in a diagram

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High pressure, low temperature: **solid phase**
High temperature, low pressure : **vapour phase**
In between : **liquid phase**

solid \rightleftharpoons liquid
liquid \rightleftharpoons vapour
vapour \rightleftharpoons solid

Solid \rightleftharpoons liquid \rightleftharpoons vapour

Source:http://abyss.uoregon.edu/~js/glossary/triple_point.html

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Application of Gibb's phase rule $F = C - P + 2$ to 1-component system:

Water system

When only 1 phase is present :

$C = 1, P = 1; F = 2$; Temperature and Pressure can be varied independently

Bivariant system

When 2 phases are in equilibrium:

$C = 1, P = 2; F = 1$; Temperature or Pressure can be varied independently

Univariant system

When all 3 phases are in equilibrium:

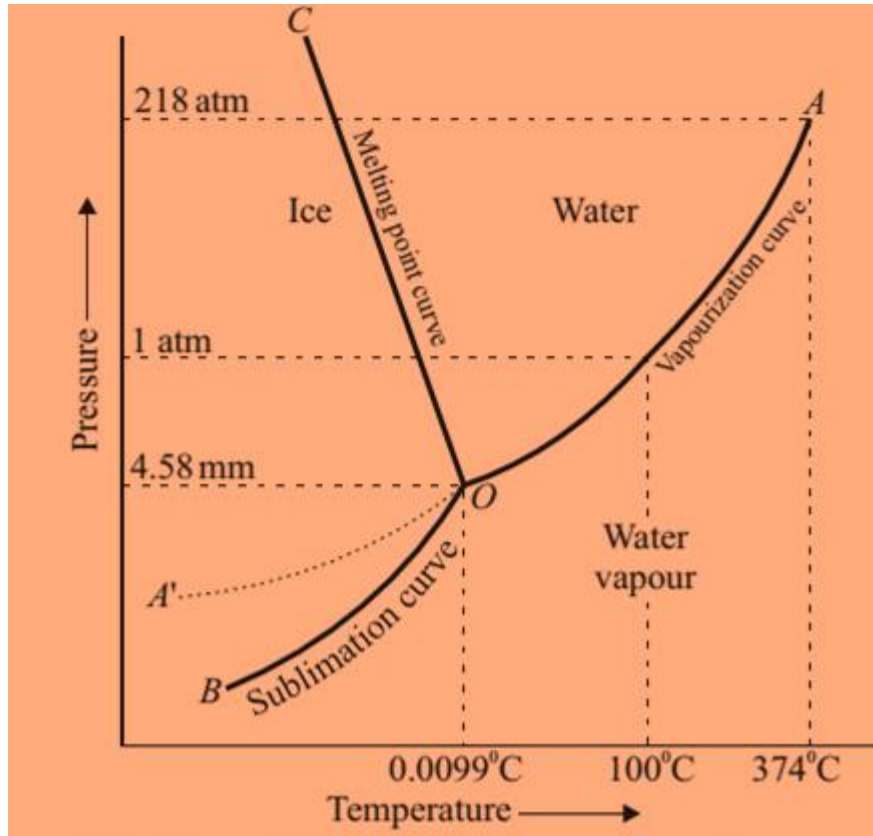
$C = 1, P = 3; F = 0$; Neither Temperature nor Pressure can be varied

Invariant system

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Phase diagram of water



OC : Melting point curve

OA : Vaporisation curve

OB : Sublimation curve

O: Triple Point

A: Critical point

OA': Metastable equilibrium

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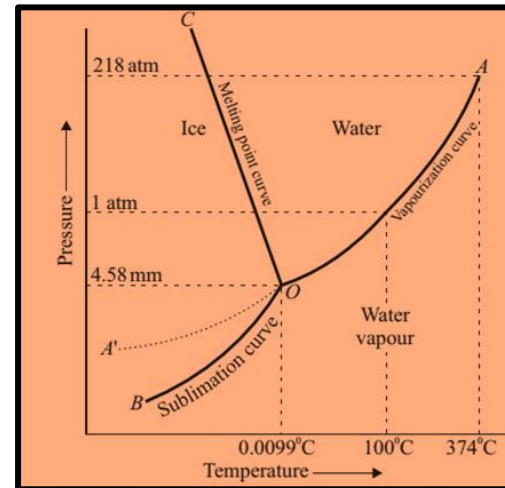
Equilibrium between solid and liquid (fusion curve OC)

- ice \rightleftharpoons water
- $F=1$, monovariant system
- variation of melting point of ice with pressure
- **slope is negative**; as ice melts its volume decreases or density increases
- Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{\text{Fusion}}}{T\Delta V} = \text{negative}$$

Where,

ΔV = decrease in volume as ice melts is -ve; ΔH_{fusion} = endothermic, +ve



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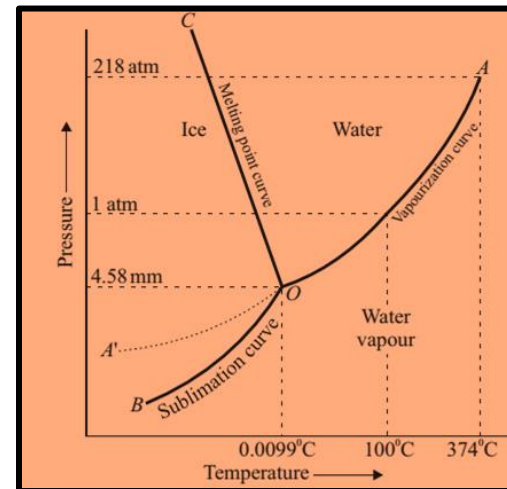
Equilibrium between solid and vapour (sublimation curve OB)

- ice \rightleftharpoons water vapour
- $F=1$, monovariant system
- variation of sublimation temperature of ice with pressure
- slope is positive
- Clausius Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{sub}}{T\Delta V} = \text{positive}$$

Where ,

ΔV = Increase in volume as ice sublimates ,+ve ; $\Delta H_{sublimation}$ = endothermic reaction, +ve



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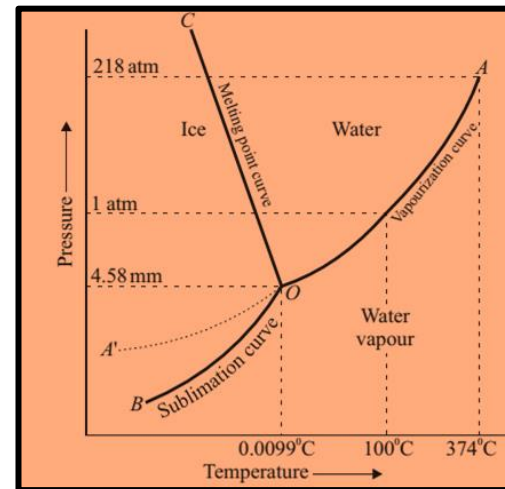
Equilibrium between liquid and vapour (vaporization curve OA)

- liquid water \rightleftharpoons vapour
- $F=1$, monovariant system
- variation of boiling temperature of water with pressure
- slope is positive
- Clausius - Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vapourisation}}}{T\Delta V} = \text{positive}$$

Where,

ΔV = Increase in volume as liquid water vapourises, +ve; $\Delta H_{\text{vapourisation}}$ = endothermic reaction, +ve



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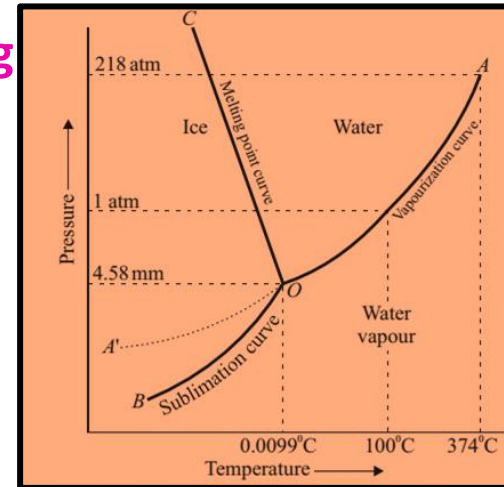
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Triple point “O”:

- Represents equilibrium between liquid, vapour and solid water (ice)
- All three phases are present together
- $F = 0$, **invariant system**
- Triple point for water lies at **0.0098°C and 4.58 mmHg**

Critical point “A”:

- the interface between liquid water and water vapour vanishes
- a point above which water does not exist in liquid state
- Critical point lies at **374°C and 218 atm** pressure

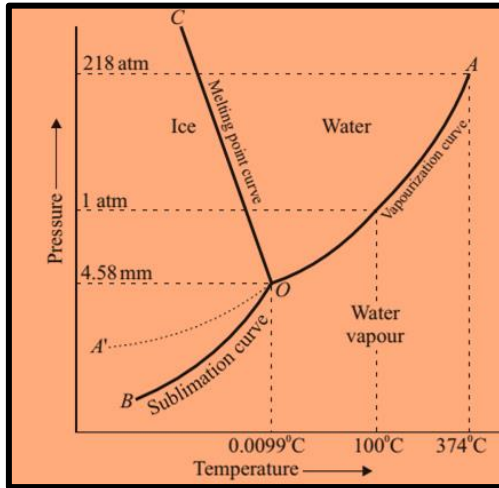


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Metastable equilibrium (OA'):

- Ice fails to form at the triple point and water continues to exist in liquid phase
- The vapour pressure of the liquid continues along OA'
- This is called **super cooled water** and represents metastable equilibrium involving liquid and vapour phases.
- Any disturbance will cause the system to go back to stable equilibrium (OB)
- The vapour pressure of the system in the metastable region is more than that of the stable system ice at the same temperature





THANK YOU

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