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Military Institute of Science and Technology

Fundamentals of Chemistry

CHEM 101

Phase

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Phase

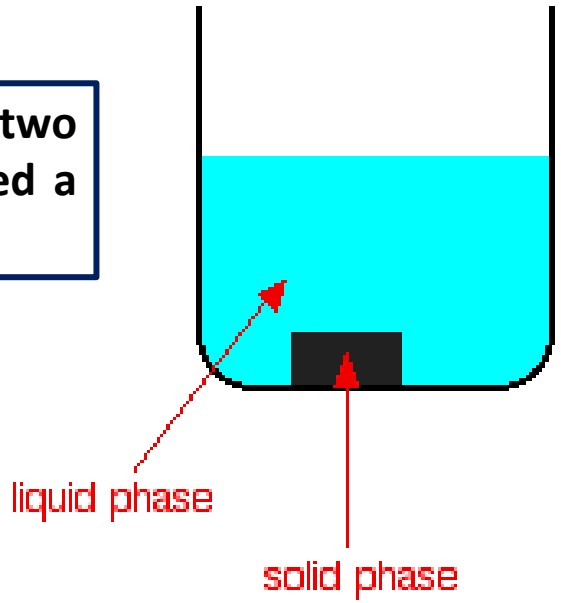
What is Phase?

Homogenous Part of a heterogenous system which is chemically uniform but mechanically separable having a definite boundary

A system consisting of two or more phases is called a heterogeneous system.

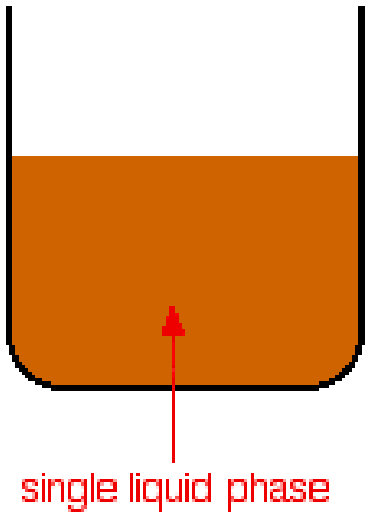
Two phases

P = 2



One phase

P = 1



A system consisting of one phase only is called a homogeneous system.

Understanding Phases

Pure substances: A pure substance (solid, liquid, or gas) made of one chemical species only, is considered as one phase. Thus oxygen (O_2), benzene (C_6H_6), and ice (H_2O) are all 1-phase systems.

Mixtures of gases: Any mixture of gases, say O_2 and N_2, is a 1-phase system.

Miscible liquids: A solution of ethanol and water is a 1-phase system.

Non-miscible liquids: A mixture of chloroform ($CHCl_3$) and water constitutes a 2-phase system.

Aqueous solutions: Aqueous solution of sodium chloride/sugar is uniform and thus 1-phase system.



A saturated solution of sodium chloride in contact with excess solid sodium chloride is a 2-phase system.

Understanding Phases

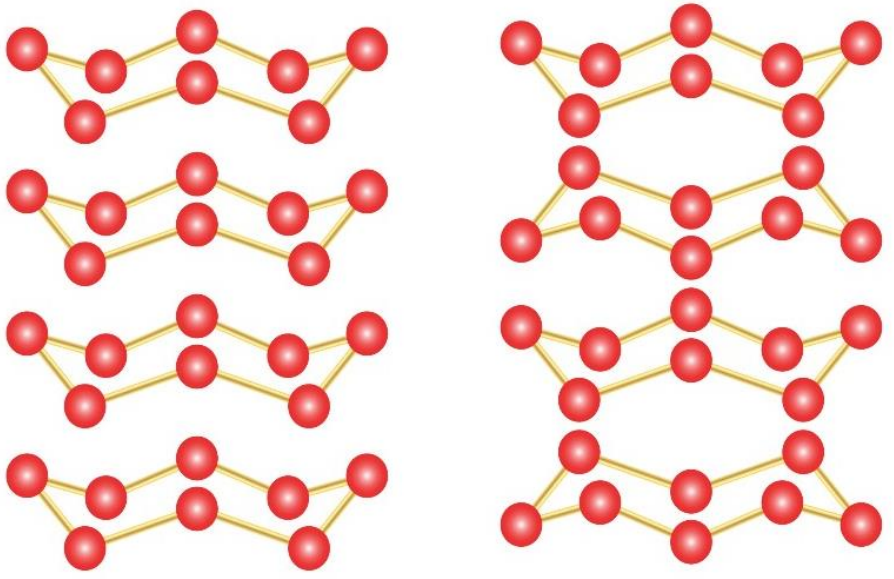
Mixtures of solids: Ordinary sulphur as it occurs in nature is a mixture of monoclinic and rhombic sulphur. These allotropes of sulphur consist of the same chemical species but differ in physical properties. Thus mixture of two allotropes is a **2-phase** system.

A mixture of two or more chemical substances contains as many phases.

Decomposition of Calcium carbonate

$$\underset{\text{(solid)}}{CaCO_3} \rightleftharpoons \underset{\text{(solid)}}{CaO} + \underset{\text{(gas)}}{CO_2}$$

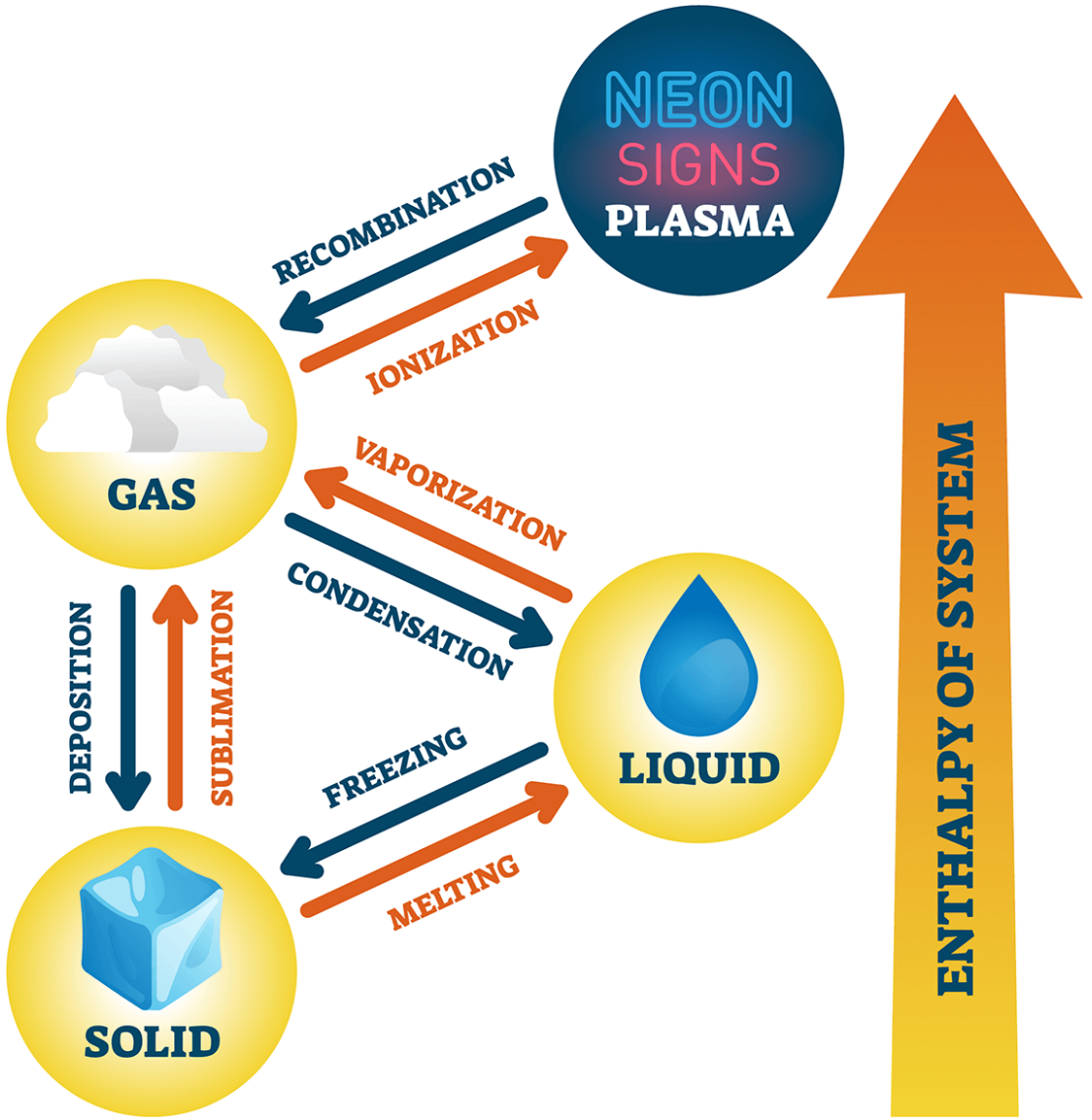
It is a 3-phase system



Rhombic Sulfur Monoclinic Sulfur

Change of Phases

Water



Phase Terms

COMPONENTS

A component in a phase refers to a **pure substance or a chemical species** that is present in the phase.

Or, **minimum number** of chemical constituents sufficient for determining the composition of all phases of a system.

Water system has three phases :
Ice, water, and water vapour. The composition of all the three phases is expressed in terms of one chemical individual H_2O. Thus, water system has one component only.

Sulphur system has four phases :
Rhombic sulphur, monoclinic sulphur, liquid sulphur and sulphur vapour. The composition of all these phases can be expressed by one chemical individual sulphur (S). Hence, it is a 1-component system.

Water and sulphur systems are 1-component systems.

Phase Terms

DEGREES OF FREEDOM

The minimum number of independently variable factors such as temperature, pressure and concentration which must be required to define the system completely

It is also known as **variance**

A system with $F = 0$ is known as **nonvariant** or having no degree of freedom.
A system with $F = 1$ is known as **univariant** or having one degree of freedom.
A system with $F = 2$ is known as **bivariant** or having two degrees of freedom.

Derivation of Phase Rule

Let us, Consider a heterogenous system consisting of P (P_1, P_2, P_3, P_4.....P) no of phases and C (C_1, C_2, C_3.....C) number of components of equilibrium

(a) *Total number of variables required specifying the state of system:*

(i) Temperature: same for all phases

(ii) Pressure: same for all phases

(iii) Concentration

Independent concentration variables for one phase with respect to the C components $= C - 1$ [$\because$ Conc. of last component is independent]

$\therefore$ Independent concentration variables for P phases with respect to the C components $= P(C - 1)$

$$\textit{Total number of variables} = P(C - 1) + 2 \qquad \ldots(1)$$

Derivation of Phase Rule

(b) *The total number of equilibria:*

The various phases present in the system can remain in equilibrium only when the *chemical potential* (μ) of each component is the same in each phases, *i.e.*

$$\begin{array}{lllllllll}
\mu_1, P_1 & = & \mu_1, P_2 & = & \mu_1, P_3 & = & \ldots & = & \mu_1, P \quad \text{Component 1} \\
\mu_2, P_1 & = & \mu_2, P_2 & = & \mu_2, P_3 & = & \ldots & = & \mu_2, P \quad \text{Component 2} \\
\vdots & & \vdots & & \vdots & & & & \vdots \\
\vdots & & \vdots & & \vdots & & & & \vdots \\
\vdots & & \vdots & & \vdots & & & & \vdots \\
\mu_C, P_1 & = & \mu_C, P_2 & = & \mu_C, P_1 & = & \ldots & = & \mu_C, P \quad \text{Component C}
\end{array}$$

(a) For each component the no of equilibria for P phases $= (P - 1)$

(b) For C component the no of equilibria for P phases $= C(P - 1)$

Total no. of equilibria involved $(E) = C(P - 1)$ ...(2)

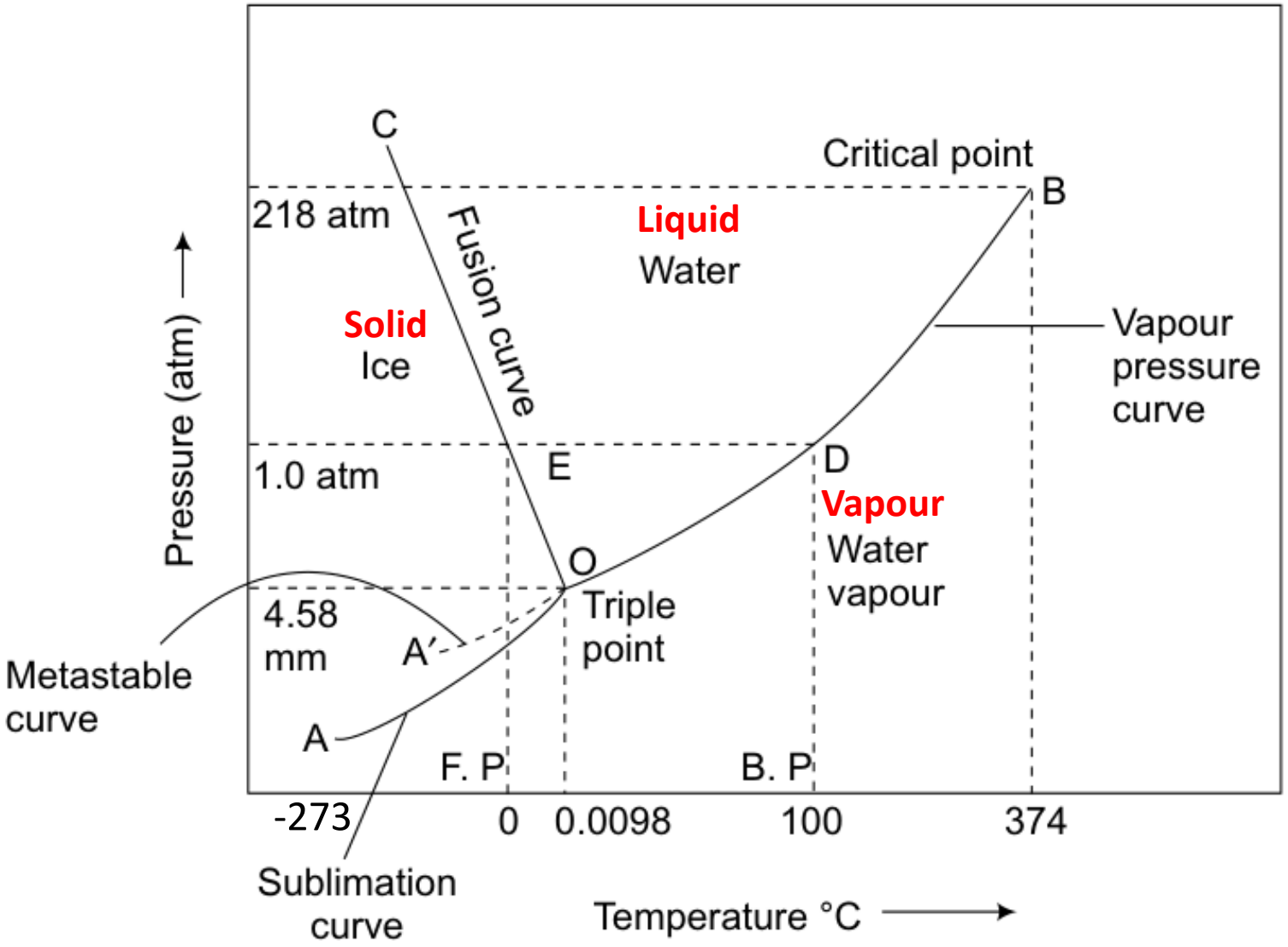
Derivation of Phase Rule

$$
\begin{aligned}
F &= \text{No. of variables} - \text{Number of equations} \\
&= [P(C-1)+2] - [C(P-1)] \\
&= PC - P + 2 - PC + C \\
&= C - P + 2 \\
F &= C - P + 2
\end{aligned}
$$

F = C – P + 2

F = Number of degree of freedom
C = Number of components
and P = Number of phases

Phase diagram of H_2O



Areas, Curves, Triple point

Areas/Regions

Solid **Liquid** **Vapour**

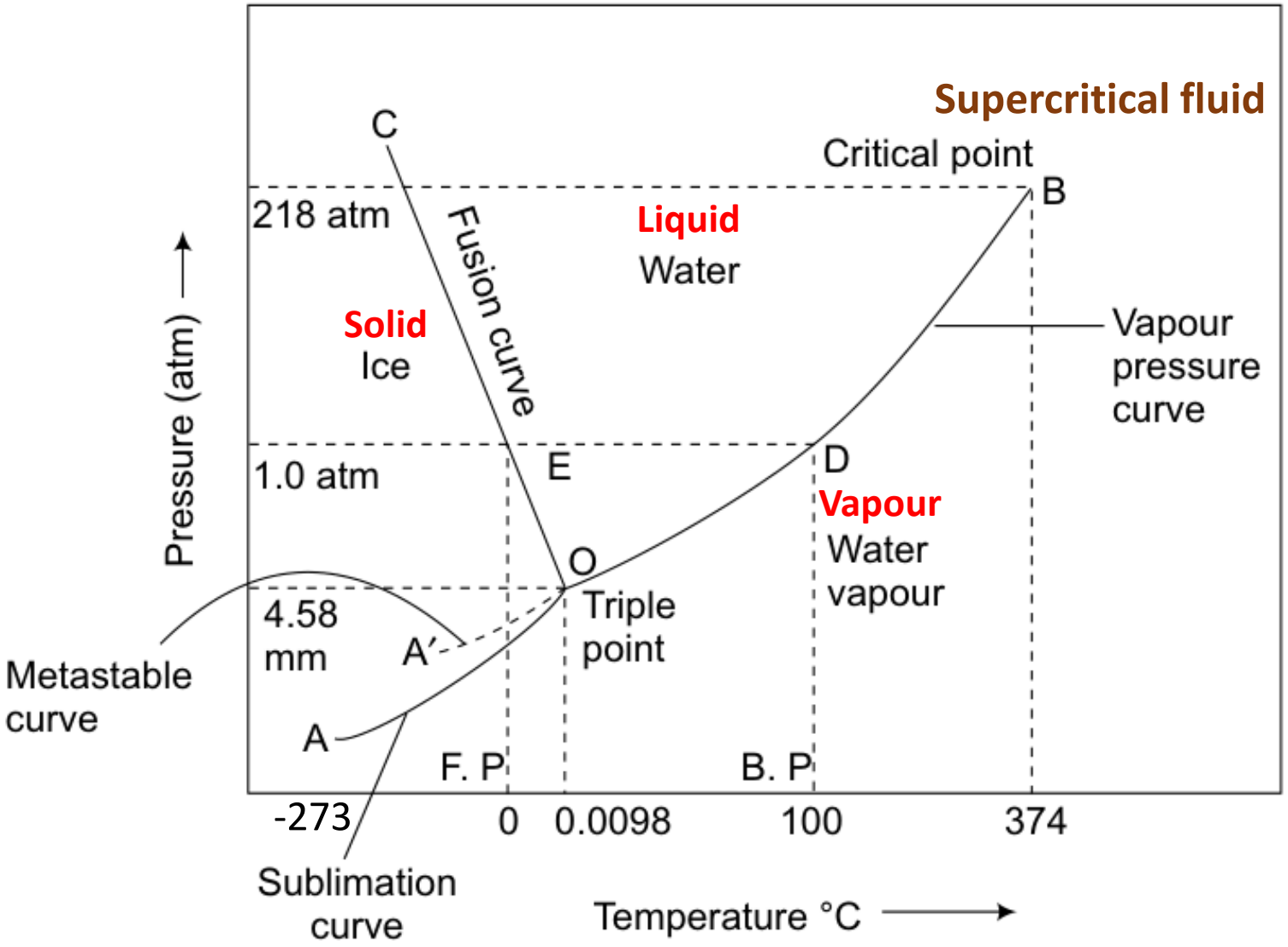
When only one phase is present

F = 1 – 1 + 2 = 2

Each single phase has two degrees of freedom

That means, each area of phase diagram represents a bivariant system.

Phase diagram of H_2O



Curves

3 Stable Curves

- Fusion/Melting Curve (OC)

  Water ⇌ Liquid

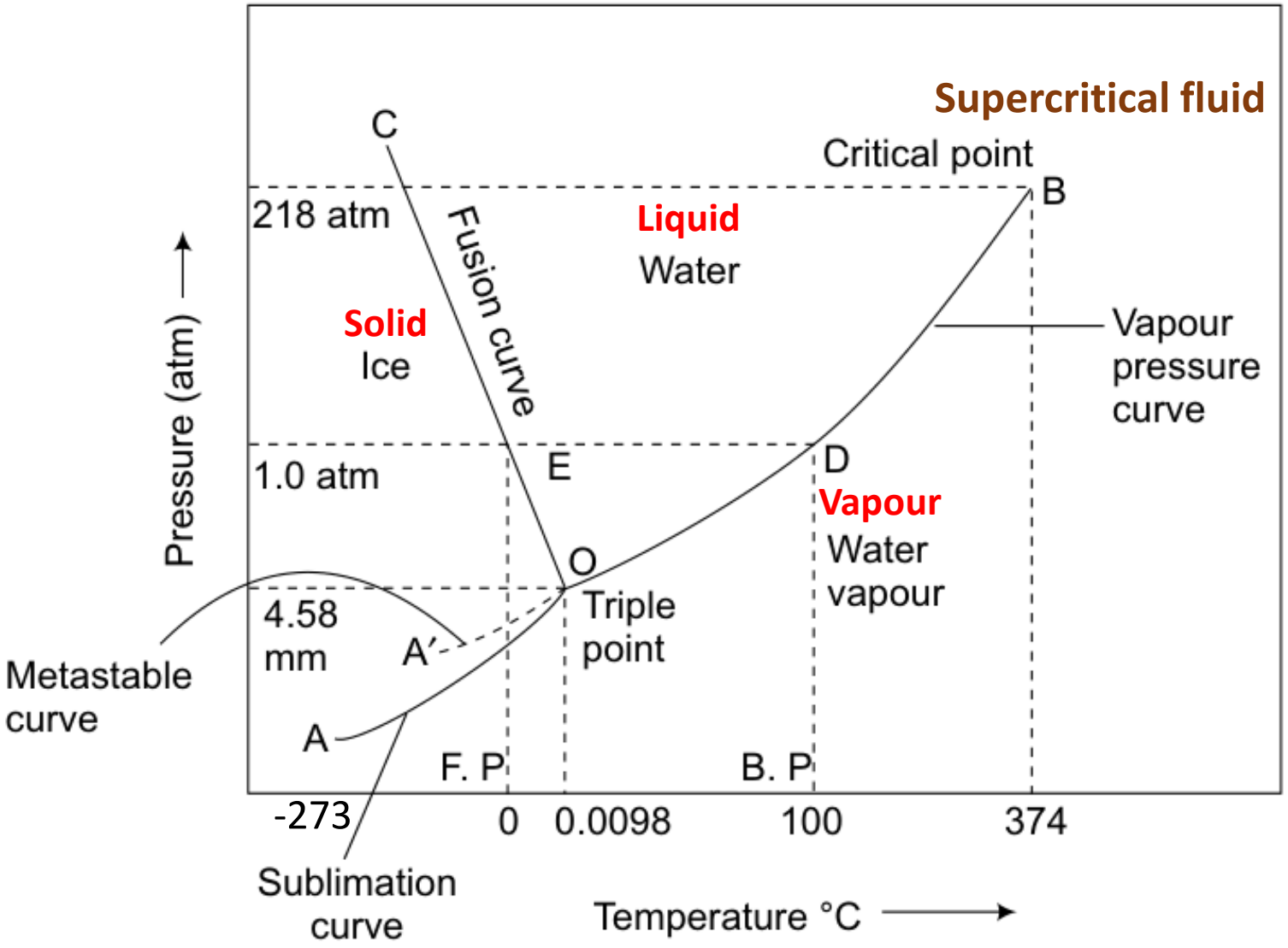
- Vaporization Curve (OB)

  Water ⇌ Vapour

- Sublimation Curve (OA)

  Ice ⇌ Vapour

Phase diagram of H_2O



Curves

Boiling Point

- At point D,

  Vapour pressure = atm pressure

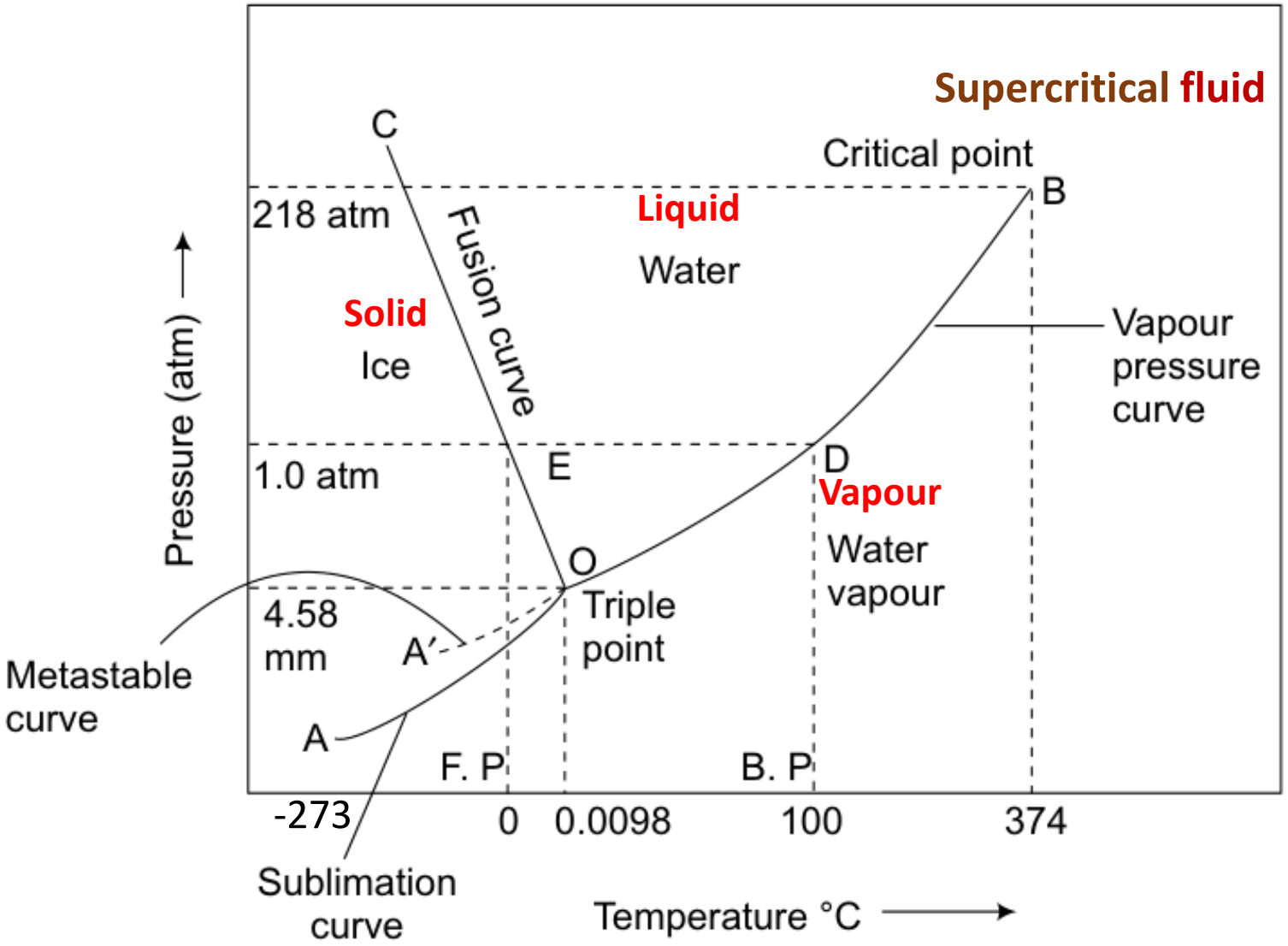
Critical Point

- At point B,

  Liquid and gas phase indistinguishable

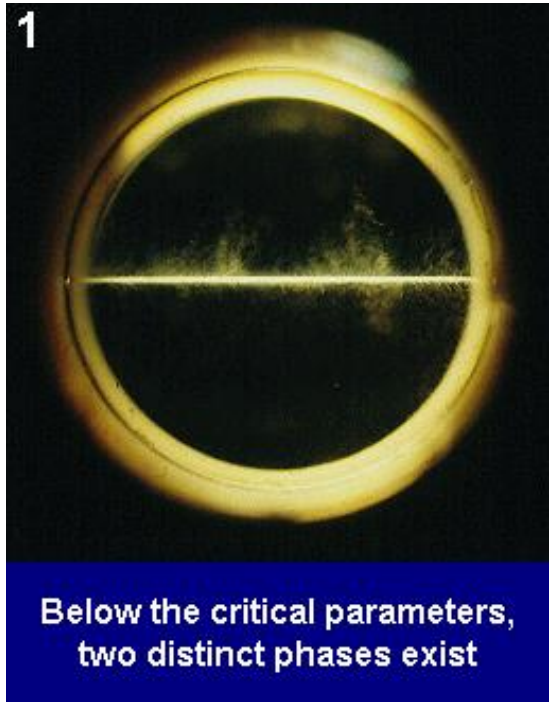
  Only one phase

Phase diagram of H_2O

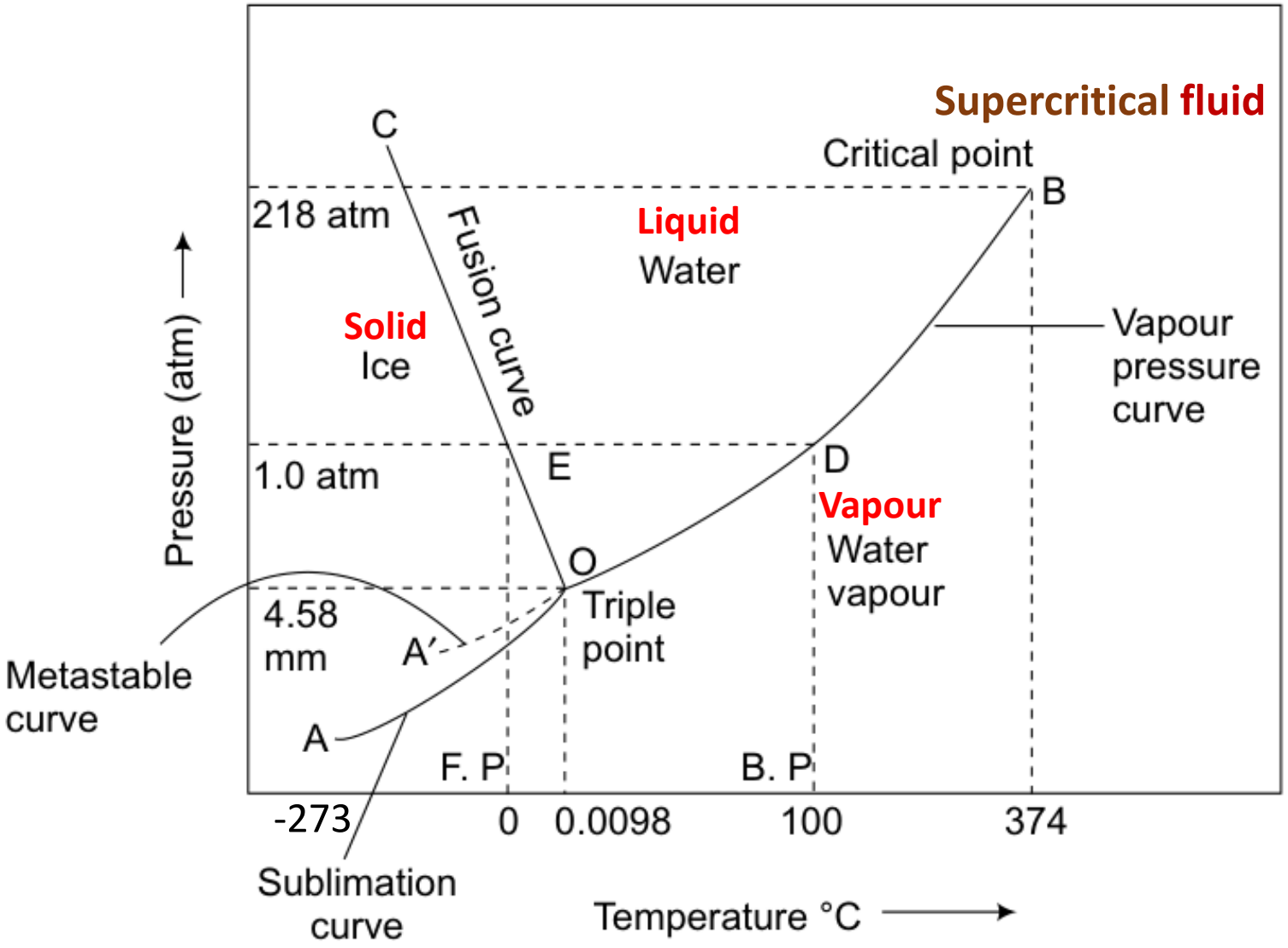


Curves

Beyond the critical point, the substance exists only as a **supercritical fluid**, which exhibits properties of both a gas and a liquid.



Phase diagram of H_2O



Curves

Triple Point

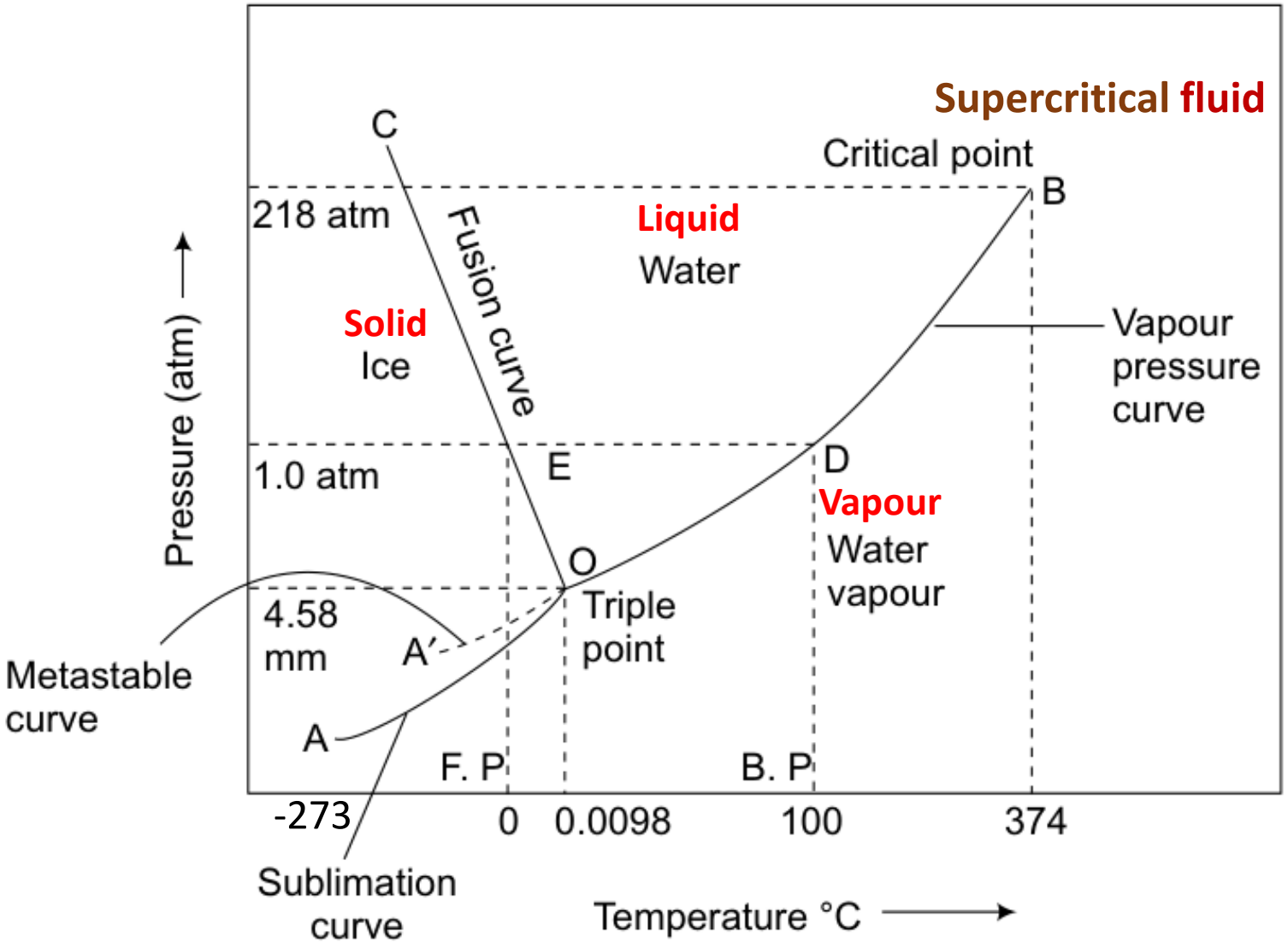
The conditions under which all the three phases (solid, liquid, vapour) can co-exist in equilibrium.

$$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

$$\mathbf{F = C - P + 2 = 1 - 3 + 2 = 0}$$

At the triple point both pressure and temperature on the diagram are fixed and, therefore, the system is nonvariant.

Phase diagram of H_2O



Curves

Metastable Curve

Careful cooling of the liquid under conditions that crystals do not form, the curve BO can be extended to A'.

This means that the liquid can be cooled far below the freezing point or ‘supercooled’

