APPLIED CHEMISTRY

Phase Rule

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LEARNING OUTCOMES

By the end of this session participants should be able to:

Understand and Interpret

- ✓ The concept and utility of phase diagrams.
- ✓ One component system
- ✓ Water system

Outline : Lecture 2

- Phase Diagram: Introduction and Definition
- One component system
- Water System

Phase Rule

Phase Diagram

Definition: A diagram which shows the conditions of equilibrium between phases of a heterogeneous system is called a phase diagram. The phase diagram is a graphical representation obtained by plotting one degree of freedom against another.

Types of phase diagram

i. P-T Diagram

If the phase diagram is plotted between **pressure** and **temperature**, the diagram is called a P-T diagram and is applied for **one component systems**.

ii. T-C Diagram

If the phase diagram is plotted between **temperature** and **composition**, the diagram is called a T–C diagram and is applied for **two component systems**.

Application

Important properties of a substance like its **melting point**, **boiling point**, **transition temperature** and **triple point** can be found with the help of a phase diagram.

Phase Rule

One component system

Water System

Water system has three phases, namely solid, liquid and vapour. Therefore three forms of equilibria:

i. **liquid** $\rightleftharpoons$ **vapour** ii. **solid** $\rightleftharpoons$ **vapour** iii. **solid** $\rightleftharpoons$ **liquid** **Each equilibria involves two phases**

Since **H_2O** is the only chemical compound involved, hence it is a **single** or **one component system**.

Applying phase rule:

$$F = C - P + 2$$

$F = 1 - P + 2 = 3 - P$, therefore, degree of freedom depends on the number of phases present at equilibrium.

The possible cases that can arise are:

i. $P = 1$; $F = 2$ (bivariant system)

ii. $P = 2$; $F = 1$ (univariant system)

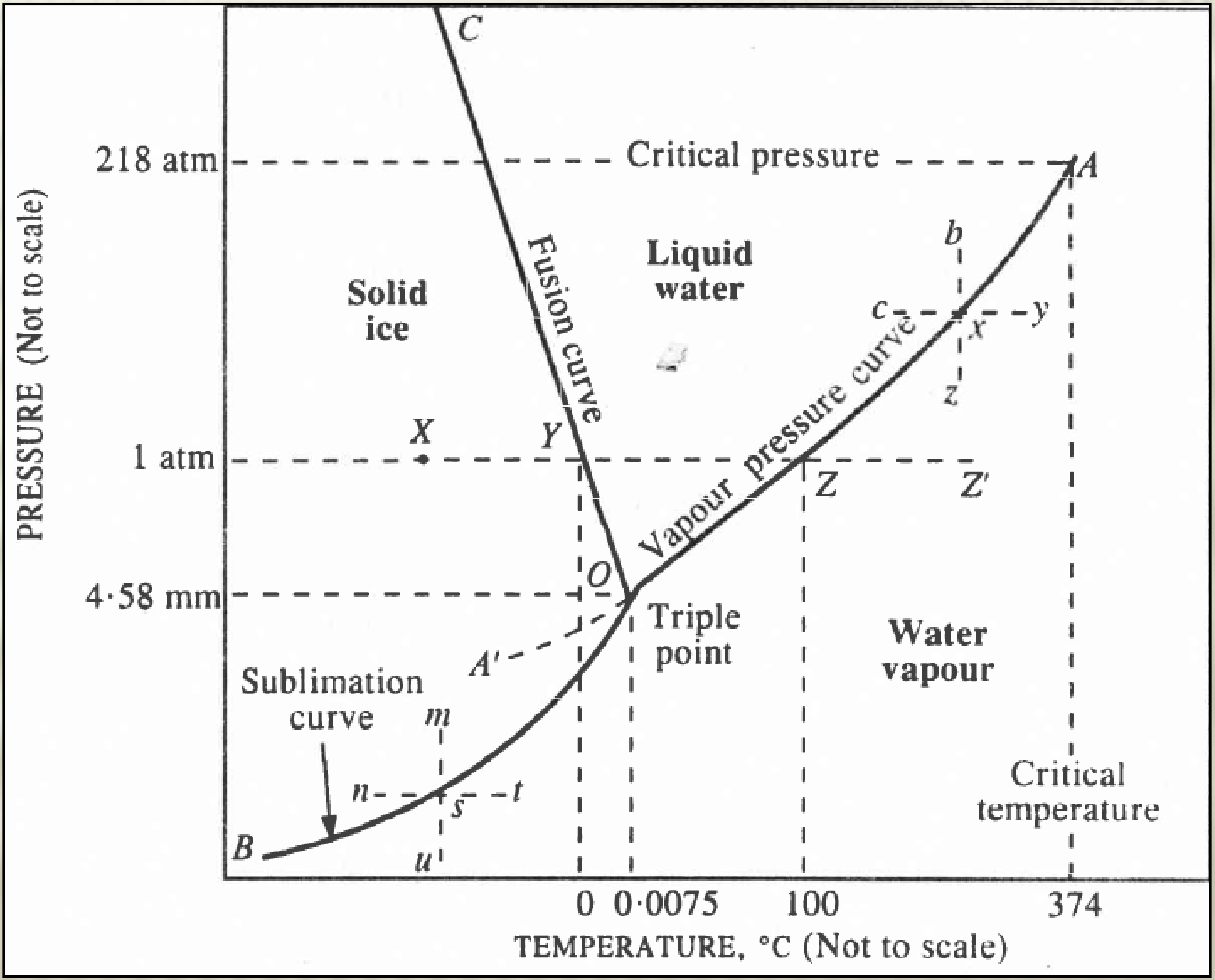
iii. $P = 3$; $F = 0$ (invariant system

Hence, for any one component system, the maximum number of degrees of freedom is two.

Therefore, such a system can be represented by two dimensional diagram.

Phase Rule

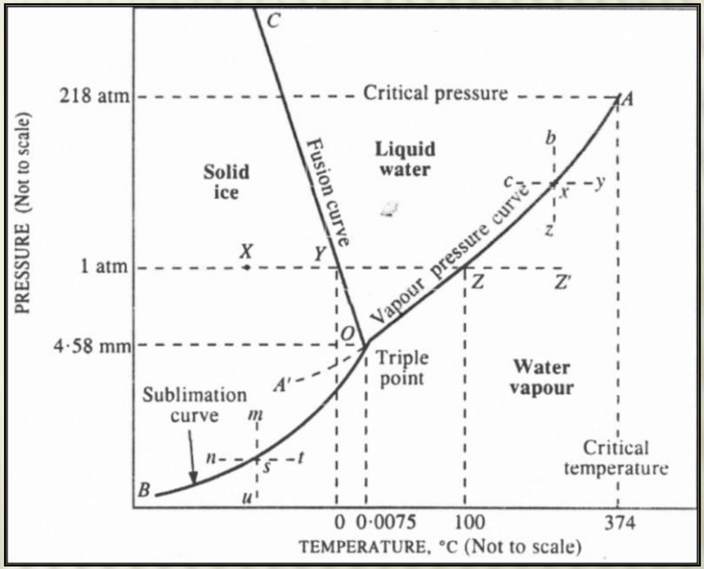
Water System



Principles of physical chemistry by Puri Sharma Pathania

Phase Rule

Phase diagram consists of **curves**, **areas** and **points** which reveal behaviour of water system.



Curves

- **There are three curves in the phase diagram. Along each curve two phases exist in equilibrium. Hence, according to the phase rule:**

  F = C – P + 2 = 1 – 2 + 2 = 1 (univariant or monovariant)

- **The system is univariant along each of these curves which means that to locate the position of any point along these curves, only one variable, either pressure or temperature needs to be specified.**

The various curves are:

Curve OA

Represents the equilibrium **H_2O (l) $\rightleftharpoons$ H_2O (g)** at different temperatures

•**Vapour pressure curve / vapourisation curve of water → vapour pressure of water at different temperatures**

•**At 100°C, vapour pressure (H_2O) = atmospheric pressure (760 mm Hg) → the boiling point of water.**

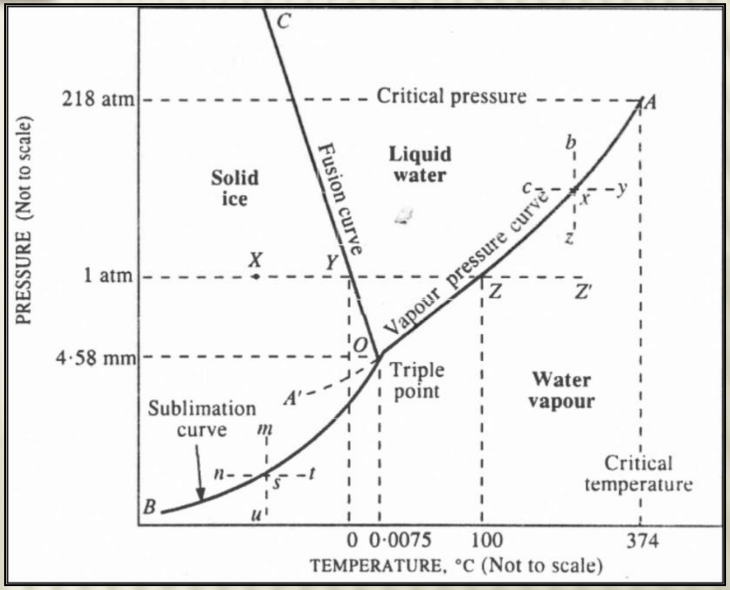
• **The curve OA extends upto critical temperature of water (374°C), as above this temperature liquid water cannot exist.**

Phase Rule

Curve OB

Represents the equilibrium:

$H_2O\ (s) \rightleftharpoons H_2O\ (g)$ at different temperatures



- Vapour pressure curve / sublimation curve of ice.
- The lower end extends upto absolute zero (-273°C) beyond which vapour phase does not exist.
- For each temperature, there can be only one pressure and vice versa

Curve OC

Represents equilibrium:

$H_2O\ (s) \rightleftharpoons H_2O\ (l)$ at all temperatures

- Fusion curve of ice → indicates the temperatures and pressures at which the solid (ice) and liquid (water) can coexist in equilibrium.
- This curve shows the effect of pressure on the melting point of ice → curve slopes towards the pressure axis which means that the melting point of ice decreases with the increase in pressure.
- Thus, while the freezing point of water at a pressure of 4.58 mm is +0.0075°C, at a higher pressure of 760 mm (i.e., 1 atm) it is reduced to O°C.

Phase Rule

Triple point

- The **point O** where all the three curves meet is known as the **triple point**.
- Represents the equilibrium:.

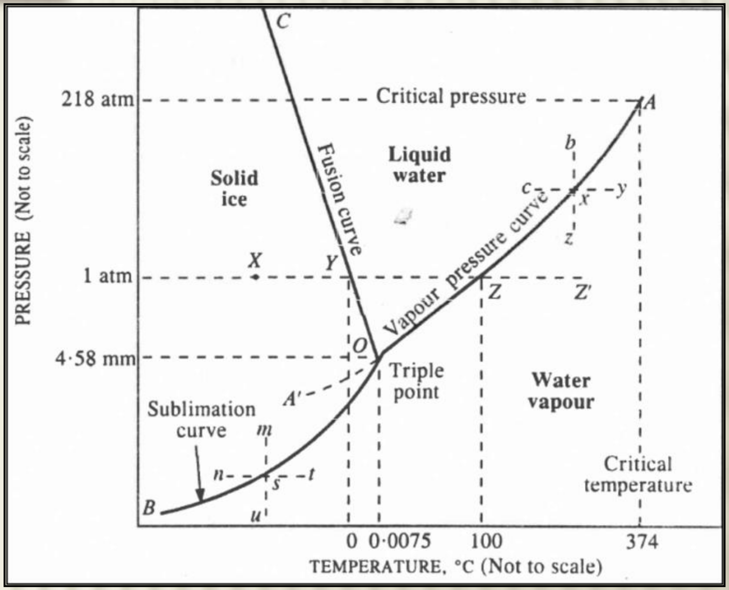
Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ Water vapor (g)

Hence, at O, P = 3, therefore

F = C – P + 2 = 1 – 3 + 2 = 0 (invariant or non-variant)

- The equilibrium is attained at a specific temperature and pressure (**0.0075 °C and 4.58 mm pressure**).

•If either pressure or temperature is varied even slightly, then at least one of the phases will disappear and all **the three phases will no longer coexist.**



Metastable curve (dotted line OA‘) – This is an extension of vaporisation curve: Water can be cooled below its freezing point without separation of ice (supercooled water). The equilibrium liquid $\rightleftharpoons$ vapour (curve OA’) is said to be meta stable equilibrium because as soon as a small particle of ice is added to supercooled liquid, the entire liquid gets solidified immediately.

Phase Rule

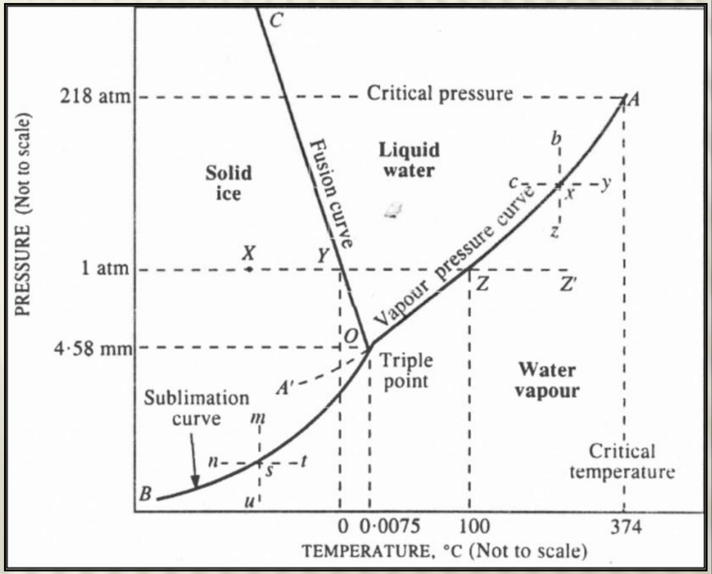
True Equilibrium	Meta stable Equilibrium
Exists when the same state in the system can be achieved from either direction	**Can be realized from one direction only**
Thermodynamically , true equilibrium is attained when the free energy content is minimum for given value of variables e.g Ice (s) $\longleftrightarrow$ water (l) at 1 atm and 0°C .	**Distributed by slight variation such as shock, stirring, etc e.g Water (l) $\longleftrightarrow$ water vapour(g) at -5 °C.**

Triple point	Critical point
The triple point of a substance is the unique temperature and pressure at which the three phases (gas, liquid and solid) of that substance coexist in thermodynamic equilibrium i.e., C=1; P=3; F = 1-3+2 =0	**A point on a phase diagram at which both the liquid and gas phases of a substance have the same density, and are therefore indistinguishable.** P = 2; C = 1; F = C – P + 2 = 1 -2 + 2 =1

Phase Rule

Areas

➢There are three areas in the phase diagram: COB, AOC and AOB consisting of ice, liquid water and water vapour, respectively.



➢All three areas consist of single phase only, Hence to apply phase rule:

F = C – P + 2 = 1 – 1 + 2 = 2 (bivariant)

➢The system is bivariant in each of the areas means that to specifically find the position of any point, it is mandatory to specify both the variables (temperature and pressure) along each of these curves which means that to locate the position of any point along these curves, only one variable, either pressure or temperature needs to be specified.

Phase Rule

System	Region	Phases in Equilibrium	Degree of freedom
Areas	AOC	One - Water	F=1-1+2 = 2 (bivariant)
	COB	One - Ice	
	AOB	One – Vapour	
Curves	OA	Two- water and vapour	F=1-2+2 = 1 (univariant)
	OA`	Two- water and vapour	
	OB	Two- Ice and Water	
	OC	Two - Ice and Water	
Point	O	Three- Ice, water & Vapour	F = 1-3+2 = 0 (invariant)

THANK YOU