

# APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 7



SCHOOL OF  
ENGINEERING AND  
TECHNOLOGY



# PHASE RULE

- **Phase :** A phase is a homogenous, physically distinct and mechanically separable portion of a system which is separated from other parts of the system by a definite boundary.

- Examples

1. A gaseous mixture, being thoroughly miscible in all proportions constitutes one phase only.
2. If two liquids are immiscible (e.g., oil and water), they will constitute two separate phases.
3. Two miscible liquids (e.g., water and alcohol) constitute one phase only.
4. At freezing point, water consists of *three* phases.

Ice (s)  $\longleftrightarrow$  Water (l)  $\longleftrightarrow$  Water vapour (g)

5. Calcium carbonate decomposes as follows:



The above equilibrium has *three* phases (two solid and one gaseous)

- **Components:** The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation.
- **Examples**

1. Water system has three phases.



Each of these phases is a different physical form of the same chemical compound represented by  $\text{H}_2\text{O}$ . Hence, it is a one-component system.

2. The thermal decomposition of calcium carbonate involves three phases.



Phase	Components
$\text{CaCO}_3$	$\text{CaO} + \text{CO}_2$
$\text{CaO}$	$\text{CaO} + \text{CO}_2$
$\text{CO}_2$	$\text{CO}_2 + \text{CaO}$



Two component system →  $\text{CaO}$  and  $\text{CO}_2$

3. The thermal decomposition of  $MgCO_3$  is as follows:

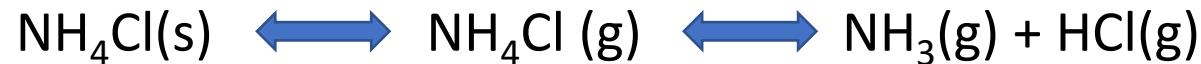


Phase	Components
$MgCO_3$	$MgO + CO_2$
$MgO$	$MgO + OCO_2$
$CO_2$	$CO_2 + OMgO$



Two component system  $\rightarrow MgO$  and  $CO_2$

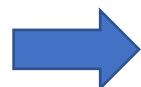
4. In the dissociation of  $NH_4Cl$  in a closed vessel, the following equilibrium occurs



Phase	Component
$NH_4Cl(s)$	$NH_4Cl$
$NH_3(g) + HCl(g)$ Equivalent quantity	$NH_4Cl(g)$
$NH_3(g) + HCl(g)$ Excess $NH_3$	$NH_4Cl(g) + NH_3(g)$
$NH_3(g) + HCl(g)$ Excess $HCl$	$NH_4Cl(g) + HCl(g)$

- In a system of sodium sulphate and water, various phases may exist like  $\text{Na}_2\text{SO}_4$ ;  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; ice, solution and vapour.

Phase	Component
$\text{Na}_2\text{SO}_4(s)$	$\text{Na}_2\text{SO}_4 + 0\text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4$ solution	$\text{Na}_2\text{SO}_4 + x\text{H}_2\text{O}$



Two component system  $\rightarrow \text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{O}$



# Degrees of freedom

- The number of degrees of freedom of a system is the minimum number of independent variables of a system, such as temperature, pressure and concentration which can define a system in equilibrium completely.
- For a system containing pure gas or only one phase, both temperature and pressure have to be defined to specify the position of the system → **DOF = 2**
- When water  $\longleftrightarrow$  water vapour, the degree of freedom is one and the system is univariant. Only one variable, either temperature or pressure is to be specified to define the position of the system → **DOF = 1**
- In a water system when all the three phases, ice, water and water vapour, are in equilibrium  
ice  $\longleftrightarrow$  water  $\longleftrightarrow$  water vapour

Three phases coexist at the freezing point of water where the temperature and pressure are automatically fixed (TRIPLE POINT= 0.01 C, 0.006 atm)) and there is no need to specify any variable  
→ **DOF = 0**

# Problems

## 1. Calculate the number of phases

- i.  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ .
- ii.  $\text{MgCO}_3(\text{s}) \rightleftharpoons \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$ .
- iii. Rhombic sulphur(s) Monoclinic sulphur(s).
- iv. Ice (s) Water (l) Water vapour (g)
- v. A system consisting of benzene and water.
- vi. Closed beaker partially filled with benzene and water.
- vii. Acetone and water.
- viii.  $\text{Fe}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{FeO}(\text{s}) + \text{H}_2(\text{g})$  equilibria.
- ix. Solution of Mohr's salt  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ .

2. Calculate the number of components present in the following systems.

- i.  $\text{Ag(s)} + \text{Ag-Pb solution(l)} + \text{Pb(s)} + \text{Ag vapour(g)}$ .
- ii.  $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{(g)} + 1/2 \text{O}_2\text{(g)}$ .
- iii.  $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{(g)} + \text{H}_2\text{O(g)}$ .
- iv.  $\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HCl(g)}$ .
- v.  $\text{NH}_4\text{Cl(s)} \rightleftharpoons x\text{NH}_3\text{(g)} + y\text{HCl(g)}$ .
- vi.  $\text{NaCl(s)} \rightleftharpoons \text{NaCl(aq)}$  or a solution of common salt.
- vii.  $\text{PCl}_5\text{(s)} \rightleftharpoons \text{PCl}_3\text{(l)} + \text{Cl}_2\text{(g)}$  at low and high temperature
- viii. A saturated solution of NaCl.

# Phase Rule

- The phase rule was given by Gibbs, 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 gravity, electrical or magnetic forces.
- The number of degrees of freedom (F), is related to the number of components (C) and phases (P) by the following phase rule equation.

$$F = C - P + 2$$

Degrees of freedom      Components      Phases



### 3. Calculate the degree of freedom in the following systems

- i.  $I_2(s) \rightleftharpoons I_2(g)$
- ii. If  $NH_4Cl(s)$  is allowed to dissociate in a vessel already containing some  $NH_3(g)$ , what is the value of the degree of freedom.
- iii. Ice and water in equilibrium
- iv. Saturated solution of NaCl
- v.  $2 KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$
- vi.  $C(s) \rightleftharpoons CO(g) \rightleftharpoons CO_2(g) \rightleftharpoons O_2(g)$
- vii.  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- viii. Mixture of water and phenol

## Solution for Q3

i.  $C = 1; P = 2$

$$F = C - P + 2; F = 1 - 2 + 2 = 1$$

ii.  $F = C - P + 2$



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

iii.  $P = 2; C = 1; F = C - P + 2; F = 1 - 2 + 2 = 1$

iv.  $C = 2, P = 3; F = C - P + 2; F = 2 - 3 + 2 = 1$

v.  $P = 3, C = 2; F = C - P + 2; F = 2 - 3 + 2 = 1$

vi. Phases = 2 (solid phase due to carbon + gaseous phase due to  $\text{CO}_2 + \text{CO} + \text{O}_2$ )  
 $C = 2$  (carbon + oxygen)

$$F = C - P + 2; 2 - 2 + 2 = 2$$

vii.  $P = 1, C = 1; F = C - P + 2 = 1 - 1 + 2 = 2$

viii.  $P = 2, C = 2; F = C - P + 2 = 2 - 2 + 2 = 2$

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# Phase diagrams/ Equilibrium diagrams

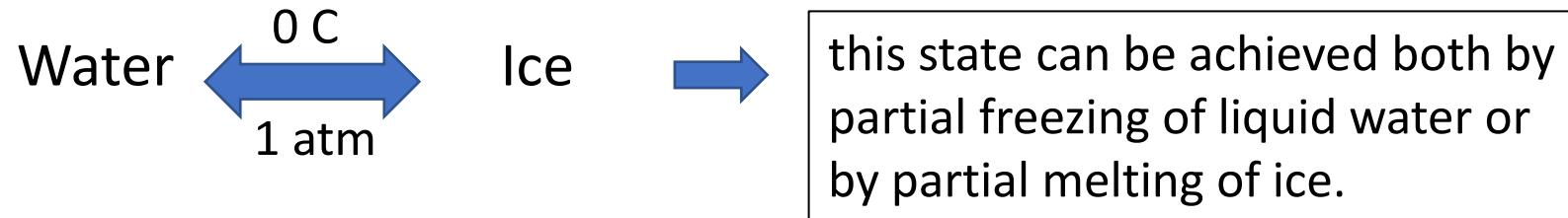
- A diagram which shows the conditions of equilibrium between phases of a heterogeneous system is called a phase diagram.
- The phase diagram is a graphical representation obtained by plotting one degree of freedom against another
- **TYPES**  
→ Temperature (T) is plotted against pressure (P), the diagram is called a **T-P diagram**  
→ Temperature (T) is plotted against composition (C), the diagram is called a **T-C diagram.**

**Importance:** 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

## TYPES OF EQUILIBRIUM

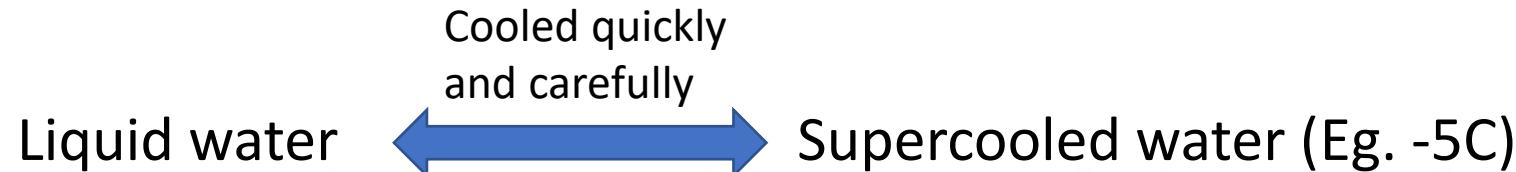
- **True Equilibrium**

- It is obtained when the free energy content of a system is minimum for a given set of variables.
- A true equilibrium exists when the same state can be approached from either direction



- **Metastable Equilibrium**

- An equilibrium which in itself is stable but becomes unstable on being disturbed by stirring or adding a piece of solid phase
- It is obtained by careful approach from one direction only



# Phase diagram for one component system

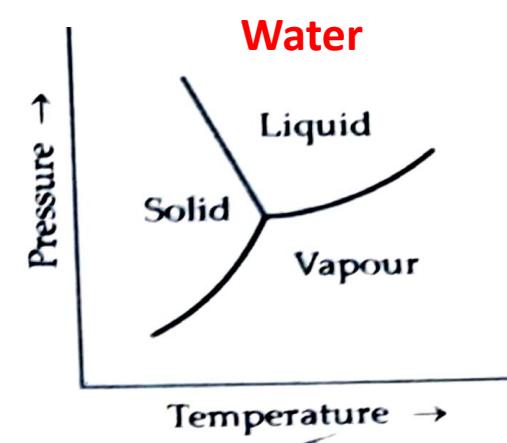
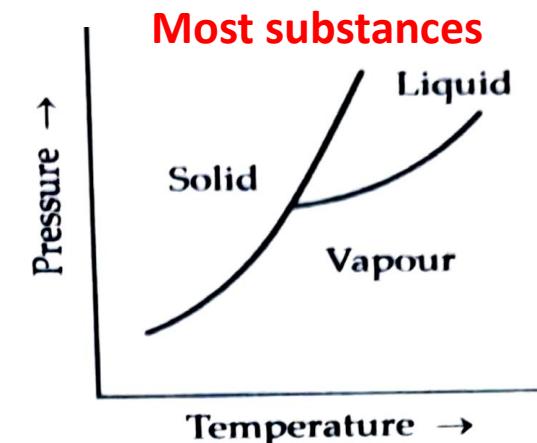
The phase diagram for system having one component can be drawn using Clausius Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

$\frac{dP}{dT}$  is variation of pressure ( $P$ ) with temperature ( $T$ ) ;

$\Delta S$  in Entropy change and  $\Delta S = (S_{final} - S_{initial})$ ;

$\Delta V$  in volume change and  $\Delta V = (V_{final} - V_{initial})$



For solid ⇌ vapour ✓ Both  $\Delta S$  and  $\Delta V$  are positive, hence  $dP/dT$  is

And liquid ⇌ vapour ✓ always positive for all substances.

→ The lines which indicate these equilibria in a P-T diagram will have positive slope

→ For solid ⇌ liquid,  $\frac{dP}{dT}$  = negative for water, positive for most substances ( $\Delta V$  = negative for water)

- According to phase rule,

$$F = C - P + 2$$

**For a one component system,  $C = 1 \rightarrow F = 1 - P + 2 = 3 - P$**

➤ When one phase is present

→  $P = 1 \rightarrow F = 3 - 1 = 2 \rightarrow$  Both temperature and pressure can be varied independently → Bivariant

→ A single phase is represented by an area

➤ When two phases are in equilibrium

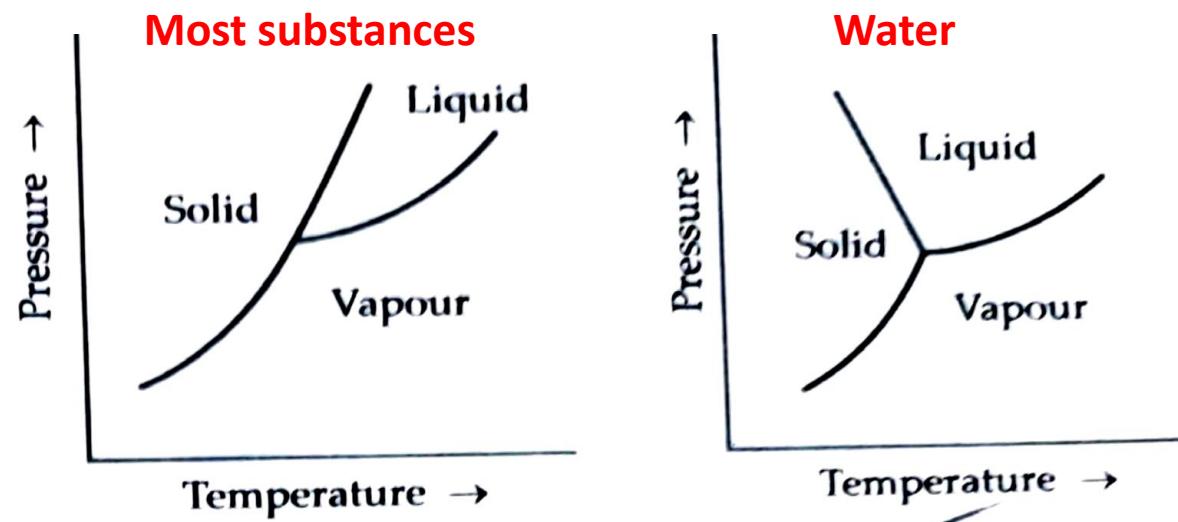
→  $P = 2 \rightarrow F = 3 - 2 = 1 \rightarrow$  Only one variable, temperature/ pressure needs to be specified → Monovariant

→ The equilibrium of two phases is represented by a line

- When three phases are in equilibrium,

$$P = 3 \rightarrow F = 3 - 3 = 0$$

- Can be established at a definite temperature and pressure → Invariant
- Equilibrium of three phases is represented by a point → Triple point



Phase diagrams for one component system

# Water System

- Water can exist in three phases: ice, water and water vapour. All these are represented by one chemical entity ( $H_2O$ ); hence  $C = 1$ .



- From the phase rule, when  $C = 1 \rightarrow F = C - P + 2 = 1 - P + 2 = 3 - P$
- Three different cases are possible:
  - (i)  $P = 1; F = 3 - 1 = 2$  (bivariant system)
  - (ii)  $P = 2; F = 3 - 2 = 1$  (univariant system)
  - (iii)  $P = 3; F = 3 - 3 = 0$  (invariant system)
- The maximum number of degrees of freedom is two, hence, the phase diagram can be conveniently represented by a two-dimensional diagram on paper using pressure and temperature as variables.

## • AREAS

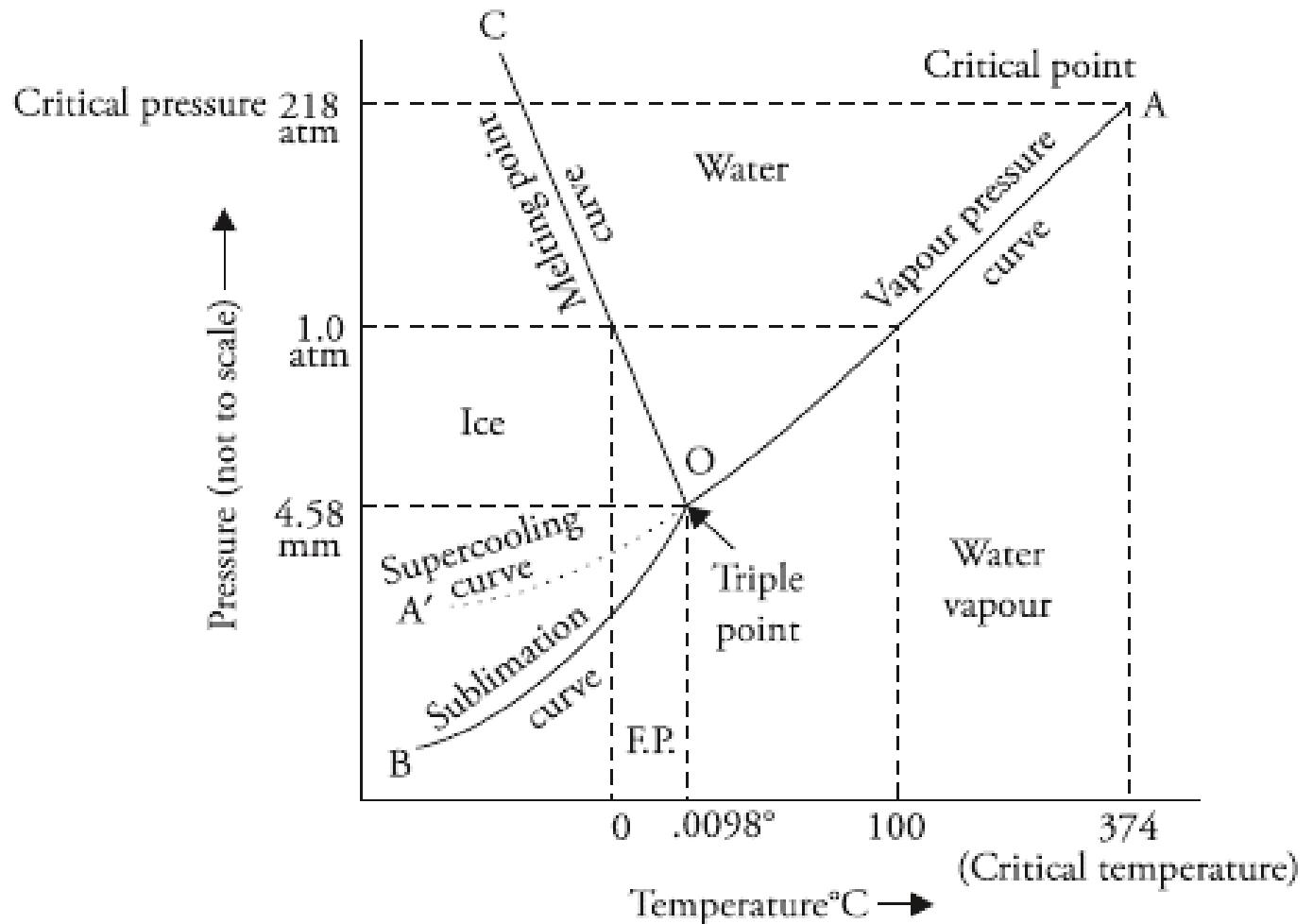
**Area BOC:** Ice

**Area AOC :** Liquid water

**Area AOB:** Water vapour

$$\rightarrow F = C - P + 2 = 1 - 1 + 2 = 2 \text{ (bivariant)}$$

→ To locate the position of any point in these areas, it is essential to specify both the variables, that is, temperature and pressure.



## • CURVES

- $F = C - P + 2 = 1 - 2 + 2 = 1$  (univariant or monovariant)
- To locate the position of any point along these curves, only one variable, either pressure or temperature needs to be specified.
- **CURVE OA:** Water  $\longleftrightarrow$  Vapour
  - This curve is known as **the vapour pressure curve of water or vaporization curve**.
  - The curve **shows the vapour pressure of liquid water at different temperatures**.
  - We can use this curve to decide how the boiling temperature varies with changing external pressure  
(At an altitude of 12 km,  $P_{ext} = 19.9$  KPa., b.p of water = 60 C)
  - **The curve has its upper limit at temperature 374 °C and pressure 218 atm → Critical Point →** beyond which the liquid phase merges into the vapour phase and they are no longer distinguishable from each other.

### • **Curve OB:** Ice $\longleftrightarrow$ Water vapour

- This curve is known as the **sublimation curve of ice**.
- It shows the vapour pressure of solid ice at different temperatures.
- The lower limit of this curve is  $-273^{\circ}\text{C}$  beyond which the vapour phase does not exist.

### • **Curve OC:** Ice $\longleftrightarrow$ Water

- This curve is known as the **fusion or melting curve of ice**.
- This curve **shows how the melting point of ice varies with pressure**.
- The curve slopes down from left to right  $\rightarrow$  melting point of ice decreases with the increase in pressure.
- **Reason for negative slope:** Ice has an open cage structure held by hydrogen bonds. On melting, this structure collapses and water has a lower volume and higher density.

- **Metastable curve OA'**

- Continuation of the vaporisation curve OA and represents the vapour pressure curve of supercooled water
- Equilibrium is said to be metastable because it can be achieved only by carefully cooling water below O.
- If an ice crystal is added to this system, then immediate solidification occurs and the temperature rises to 0 °C

- **TRIPLE POINT:** Ice  $\longleftrightarrow$  Water  $\longleftrightarrow$  Water vapour

- $F = C - P + 2 = 1 - 3 + 2 = 0$  (invariant or non-variant)
- The equilibrium is attained at a specific temperature and pressure (0.0098 °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.

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# Sulphur System

- It is a one-component, four-phase system. The four different phases of the sulphur system are :
  - (i) Rhombic sulphur (SR)
  - (ii) Monoclinic sulphur (SM)
  - (iii) Liquid sulphur (SL)
  - (iv) Vapour sulphur (SV)
- When  $C = 1$ , then from the phase rule equation,  $F = C - P + 2$ ;  $F = 1 - P + 2 = 3 - P$
- Different cases possible:
  - i.  $P = 1$ ;  $F = 3 - 1 = 2$  (bivariant system)
  - ii.  $P = 2$ ;  $F = 3 - 2 = 1$  (univariant system)
  - iii.  $P = 3$ ;  $F = 3 - 3 = 0$  (invariant system)
  - iv.  $P = 4$ ;  $F = 3 - 4 = -1 \rightarrow$  Not possible → all the four phases of the sulphur system can never exist in equilibrium.
- A system in which two or more solid states exist in equilibrium is called a polymorphic system.

- **AREAS**

**Area ABG:** Rhombic Sulphur

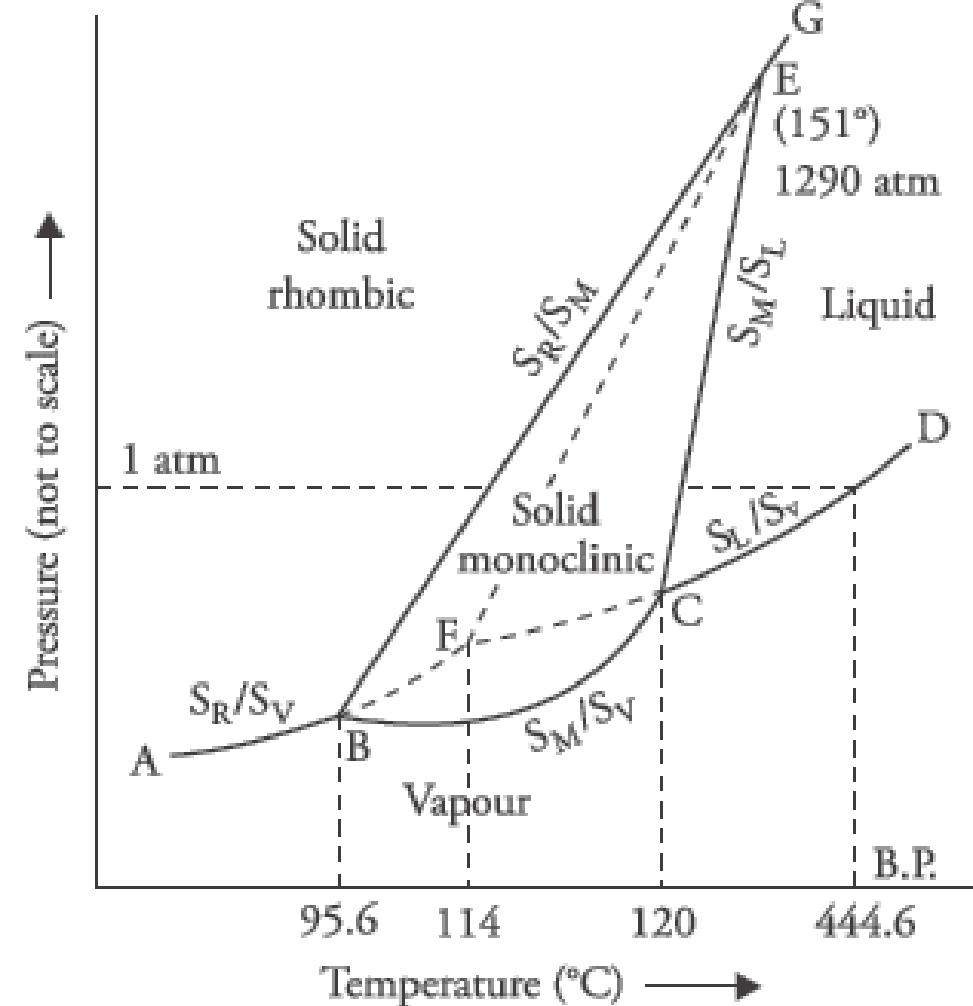
**Area BECB:** Monoclinic Sulphur

**Area GECD:** Liquid sulphur

**Area ABCD:** Vapour sulphur

For each area, C = 1; P = 1, F = 3 – 1 = 2 → bivariant

→ To locate the position of any point in these areas, both the variables—pressure and temperature—need to be specified.



## • CURVES

- **Curve AB :  $S_R \leftrightarrow S_v$**

It is the vapour pressure curve of rhombic sulphur

- **Curve BC:  $S_M \leftrightarrow S_v$**

It is the vapour pressure curve of monoclinic sulphur.

- **Curve CD:  $S_L \leftrightarrow S_v$**

• It is the vapour pressure curve of liquid sulphur.

- **Curve BE:  $S_R \leftrightarrow S_M$**

• It is the transition curve of  $S_R$  to  $S_M$ .

• Along this curve, two solid phases are in equilibrium. The line BE slopes away from the pressure axis showing that the transition temperature can be raised with increase in pressure.

- **Curve CE:**  $S_M \longleftrightarrow S_L$
- It is the fusion curve of SM.
- It represents the effect of pressure on the melting point of  $S_M$ . The melting point rises with the increase in pressure.
- The curve ends at point E because monoclinic sulphur does not exist beyond this point

• **Curve EG:**  $S_R \longleftrightarrow S_L$

- It is the fusion curve of SR.

→ Along all the six curves, two phases are in equilibrium →  $F = C - P + 2 = 1 - 2 + 2 = 1$  (univariant).

→ The system along each of these curves is univariant, hence only one variable (either pressure or temperature) is needed to express the system completely along these curves.

- **POINTS:** There are three stable triple points in the sulphur system
- **B** →  $S_R \leftrightarrow S_M \leftrightarrow S_V$  ( $95.6^\circ\text{C}$ , 0.006 mm)
- **C** →  $S_M \leftrightarrow S_L \leftrightarrow S_V$  ( $120^\circ\text{C}$ , 0.04 mm)
- **E** →  $S_R \leftrightarrow S_M \leftrightarrow S_L$  ( $151^\circ\text{C}$ , 1290 atm)
- According to the phase rule equation,  $F = C - P + 2 = 1 - 3 + 2 = 0$  (invariant or non-variant).
- **METASTABLE EQUILIBRIA** →  $F = C - P + 2 = 1 - 2 + 2 = 1$  (univariant).
- **Dashed curve BF:**  $S_R \leftrightarrow S_V$ 
  - It is the vapour pressure curve of metastable  $S_R$ .
  - If rhombic sulphur is heated rapidly, it will bypass the transition point B without changing to monoclinic sulphur

- **Dashed curve CF: Supercooled  $S_L \longleftrightarrow S_V$** 
  - It is the vapour pressure curve of supercooled liquid sulphur.
  - If liquid sulphur is cooled rapidly, it does not change to monoclinic sulphur at point C and continues to exist as supercooled liquid.
- **Dashed curve FE: Metastable  $S_R \longleftrightarrow S_L$** 
  - This is the fusion curve of metastable  $S_R$ .
- **Metastable triple point F: Metastable  $S_R \longleftrightarrow S_L \longleftrightarrow S_V$** 
  - According to the phase rule equation,  $F = C - P + 2 = 1 - 3 + 2 = 0$  (invariant)

# Two component Systems

- In a two-component system  $\rightarrow C = 2 \rightarrow F = 2 - P + 2 = 4 - P$
- When  $P = 1$ ,  $\rightarrow F = 2 - 1 + 2 = 3$  (highest)  $\rightarrow$  three variables—temperature, pressure and composition—are required to explain the system completely.
- In order to have a single-phase diagram for a two-component system, we consider any two of the three variables for graphic representation, assuming the third to be constant
  - (i) Pressure–temperature diagram (P–T) when composition is constant
  - (ii) Temperature–composition diagram (T–C) when pressure is constant
  - (iii) Pressure–composition diagram (P–C) when temperature is constant
- **Condensed System:** In the solid–liquid equilibrium, usually the gas phase is absent and the effect of pressure on the system is so small that it is neglected

**For condensed Systems  $\rightarrow F = C - P + 1$  ( REDUCED/ CONDENSED PHASE RULE)**

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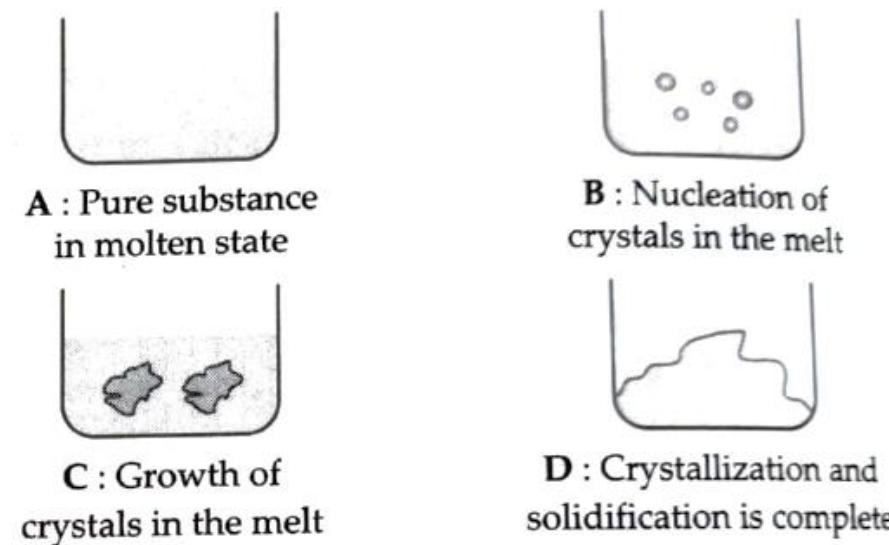
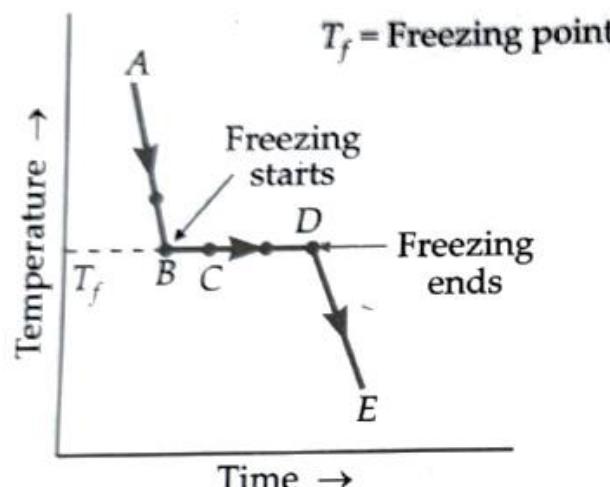
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# Construction of Phase diagrams

## THERMAL ANALYSIS/ COOLING CURVES

- Solids of different compositions are taken at a temperature above their melting points. The resulting mixture is cooled slowly and cooling curves are constructed by plotting temperature against time.
- For a mixture of definite composition, cooling curves help us to determine:
  1. Freezing point
  2. Eutectic point
- Cooling curve of a pure substance



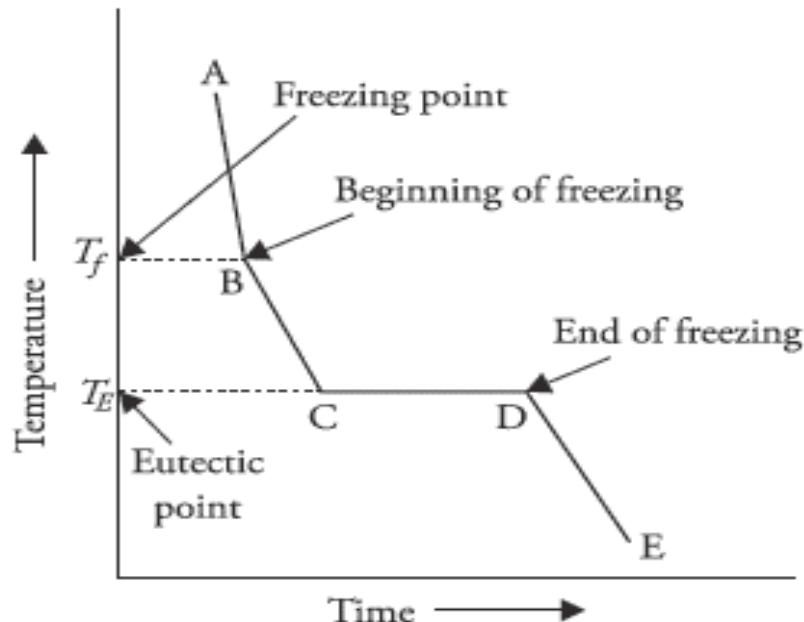
**AB:** the liquid cools and the fall in temperature is continuous

**Point B:** Start of solidification

**BD:** Solidification continues and ends at D which is end point of solidification (Temperature remains constant as heat evolved during solidification is equal the heat transferred to surroundings)

**DE:** solid cools down further till its temperature is equal to the room temperature.

- **Cooling curve of mixture of two solids**



**AB:** Smooth cooling of the mixture (solid B in solid A)

**Point B:** A starts solidifying ( $F = C+1 - P = 2 + 1 - 2 = 1$ )

→ Separation of A in solid phase changes the composition of liquid phase

→ Temperature is fixed and lower than freezing point of A as B is present and gets lower to another fixed value as separation of A continues and molality of B in solution increases.

**Point C:** B starts solidifying with A. ( $F = 2 + 1 - 3 = 0$ ) → Eutectic point

**CD:** Solidification of A and B continues

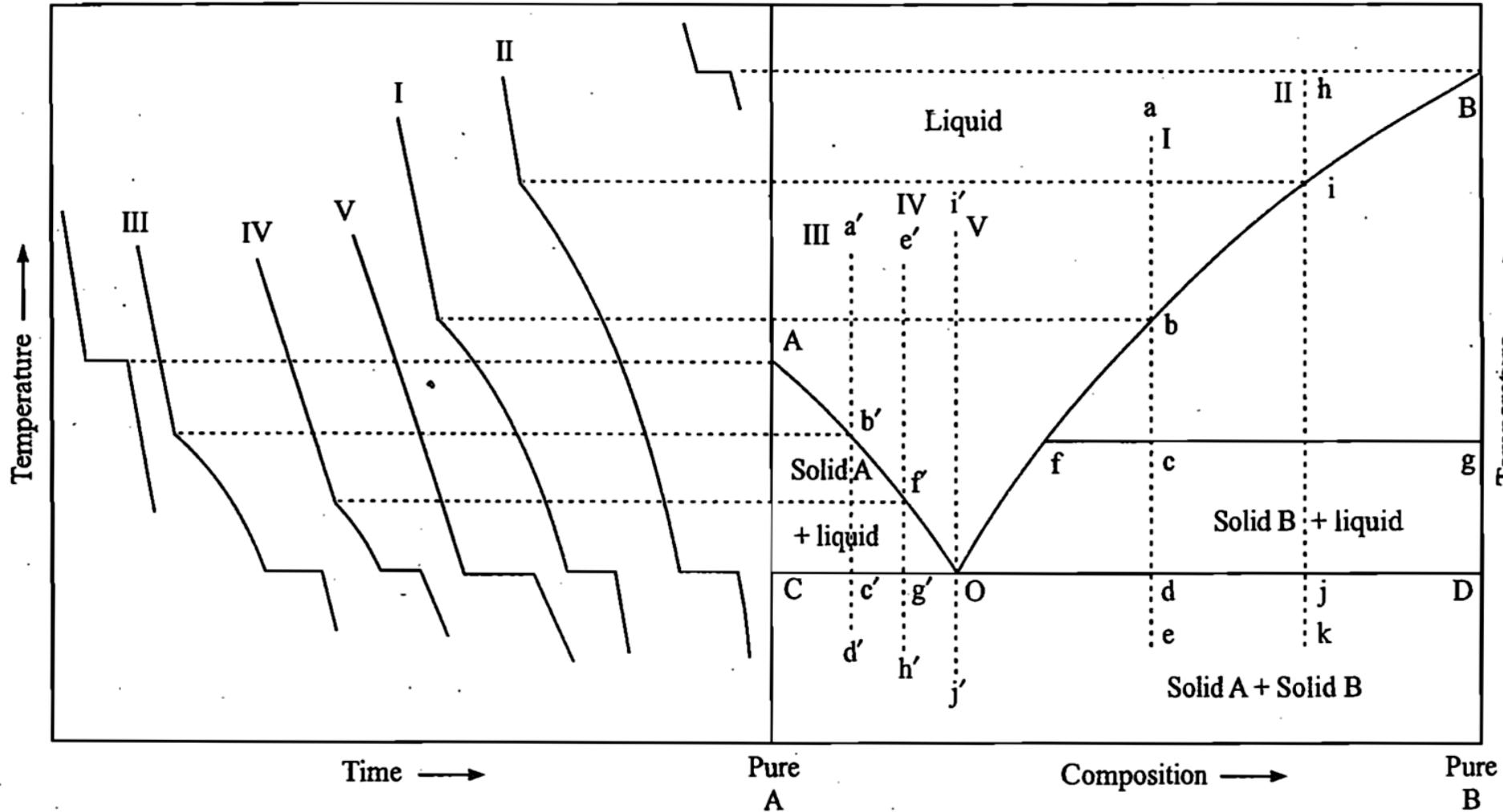
→ Temperature and composition both are fixed

→ Composition of liquid which separates out will have same composition as liquid phase.

**DE:** Cooling of the solid mixture

- **Eutectic System:** A binary system consisting of two substances which are miscible in all proportions in the liquid phase and which do not react chemically
- **Eutectic Mixture:**
  - A solid solution of two or more substances having the *lowest freezing point* of all the possible mixtures of the components
  - It melts to a liquid of the same composition
  - The eutectic mixture has a definite composition and a sharp melting point
- **Example:** → A mixture of Ag and Pb of composition 97.4% Pb and 2.6% Ag with eutectic point (freezing point) at 303 °C.
  - A mixture of Bi–Cd of composition 60% Bi and 40% Cd with eutectic point 144 °C
- **Eutectic point:** The minimum freezing point attainable corresponding to the eutectic mixture is termed as the eutectic point (lowest melting point).

# A Simple Eutectic Phase Diagram



Cooling Curves of mixtures of different compositions

Phase Diagram

III, IV → B in A

I, II → A in B

V → Eutectic composition

<i>Location of the system</i>	<i>Status of the system</i>	<i>Degrees of freedom</i>	
		<i>number</i>	<i>kind</i>
A	Freezing point of A	0	fixed $T$
B	Freezing point of B	0	fixed $T$
AO	Start of crystallization of A	1	$T$ or composition
BO	Start of crystallization of B	1	$T$ or composition
O	Eutectic point	0	fixed $T$ and fixed composition
Area above AOB	Liquid phase	2	$T$ and composition
Area below COD	Solid mixture	1	$T$
Area ACOA	Solid A in equilibrium with liquid phase whose composition lies on the curve AO.	1	$T$ or composition
Area BDOB	Solid B in equilibrium with liquid phase whose composition lies on the curve BO.	1	$T$ or composition
COD	Systems where both A and B crystallize together from liquid phase O.	0	fixed $T$ (eutectic temperature) and fixed composition (eutectic composition O)

# Expected pattern of cooling curves

## *Pure components*

Rapid cooling of liquid → Halt; solidification of the compound → Cooling of solid compound

## I, II, III, IV *Composition lying anywhere between AO or BO*

Rapid cooling of liquid → Break; solidification of A or B → Slower cooling; solidification continues

Cooling of solid mixture ← Horizontal portion; eutectic point

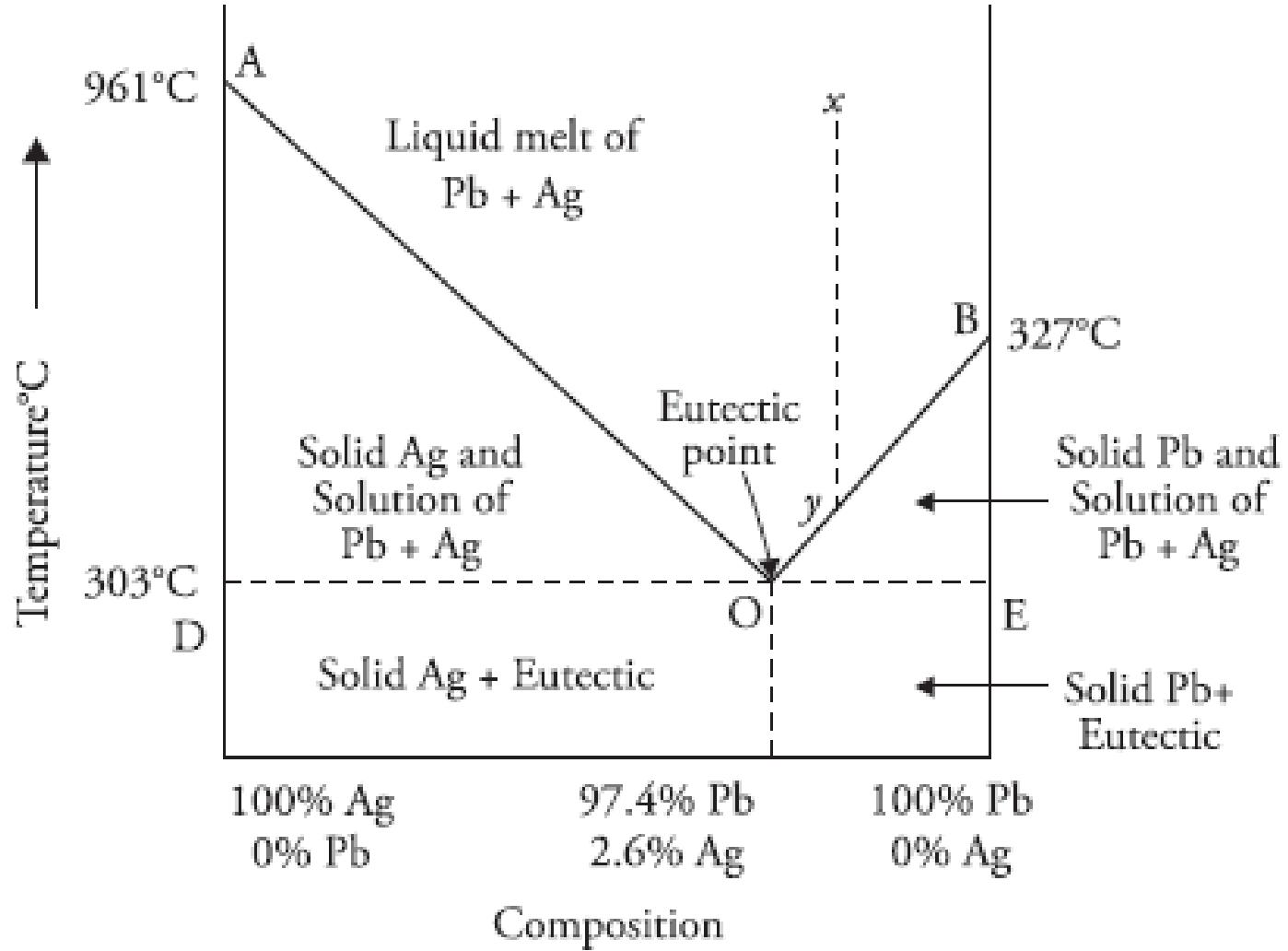
## V *Eutectic composition*

Rapid cooling of liquid → Horizontal portion; → eutectic point → Cooling of solid mixture

# Lead – Silver System

- It is a simple eutectic system → Silver and lead are miscible in all proportions and do not react chemically.
- The system consists of four phases:
  - (i) Solid silver
  - (ii) Solid lead
  - (iii) Solution of molten silver and lead
  - (iv) Vapour
- As the gaseous phase is practically absent, pressure has no effect on the equilibrium, one variable is neglected and the condensed phase rule  $F = C - P + 1$  will be applicable

# Phase diagram of lead–silver system

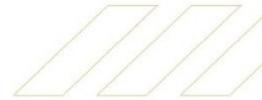


- **POINTS**

**Point A:** Melting point of pure Ag

**Point B:** Melting point of pure Pb

- At these points,  $C = 1$ ,  $P = 2$  (pure Ag in equilibrium with its liquid or pure Pb in equilibrium with its liquid); hence,  $F = C - P + 1$ ;  $1 - 2 + 1 = 0$ .



- **CURVES**

- **Addition of Pb to pure Ag lowers the melting point of Ag; similarly, addition of Ag to pure Pb lowers the melting point of Pb.**
- **Curve AO:** melting point of Ag on gradual addition of Pb. Along this curve, solid Ag and solution are in equilibrium.
- **Curve BO:** melting point of Pb on gradual addition of Ag. Along this curve, solid Pb and solution are in equilibrium.
- Along AO and BO,  $C = 2$   $P = 2 \rightarrow F = C - P + 1$  ;  $2 - 2 + 1 = 1$

## • **AREAS**

### • **Area above AOB**

- It consists of only one phase (liquid solution).
- $C = 2, P = 1 \quad F = C - P + 1 = 2 - 1 + 1 = 2 \rightarrow$  Both temperature and composition are required to be specified to define the system completely

■ **Area ADOA:** It contains two phases—solid Ag and solution containing Pb and Ag

■ **Area BOEB:** It represents the phases—solid Pb + solution containing Pb and Ag.

For both these areas,  $F = C - P + 1, \quad C = 2$  (Pb and Ag),  $P = 2$  (Liquid + solid phase),  $F = 2 - 2 + 1 = 1$

• **Area below DOE:** It represents a solid mixture of Pb or Ag with eutectic. The number of phases is 2 (either Ag or Pb + eutectic)

➤  $C = 2, P = 2 \rightarrow F = C - P + 1 = 2 - 2 + 1 = 1 \rightarrow$  system is univariant.

## • Eutectic Point O

- Three phases—solid Ag, solid Pb and the melt are in equilibrium.
- $F = C - P + 1 = 2 - 3 + 1 = 0 \rightarrow$  Invariant
- Both temperature ( $303^{\circ}\text{C}$ ) and composition (Ag 2.6% and Pb 97.4%) are fixed at this point. If the temperature is increased above the eutectic point, the solid phase (silver or lead) will disappear and if the temperature decreases below the eutectic point, the solution phase disappears and only the solid phase (eutectic + solid lead or silver) will remain.

## • Difference between melting point, triple point and eutectic point

- At melting point, a solid is in equilibrium with a liquid of the same composition.
- At triple point, three phases are in equilibrium.
- At eutectic point, two solids and a liquid are in equilibrium.

# Application of Ag–Pb system

- **Pattinson's process for desilverisation of argentiferous lead**

- Argentiferous lead is first heated to a temperature above its melting point. The system consists of only the liquid phase represented by point x
- It is then allowed to cool. The temperature of the melt will fall along the perpendicular line xy without change in composition
- As the point y is reached, lead will begin to crystallise and the percentage of silver will increase in the solution. The system moves along the curve yo
- The melt continues to be richer and richer in silver until the point O is reached. At point O, the percentage of silver is 2.6% by mass.
- After removing the lead that separates out, the liquid is cooled further to give a mixture of eutectic composition (97.4% Pb + 2.6% Ag).
- Pure silver is obtained from this alloy by other processes like cupellation.

# THANK YOU



# APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 7

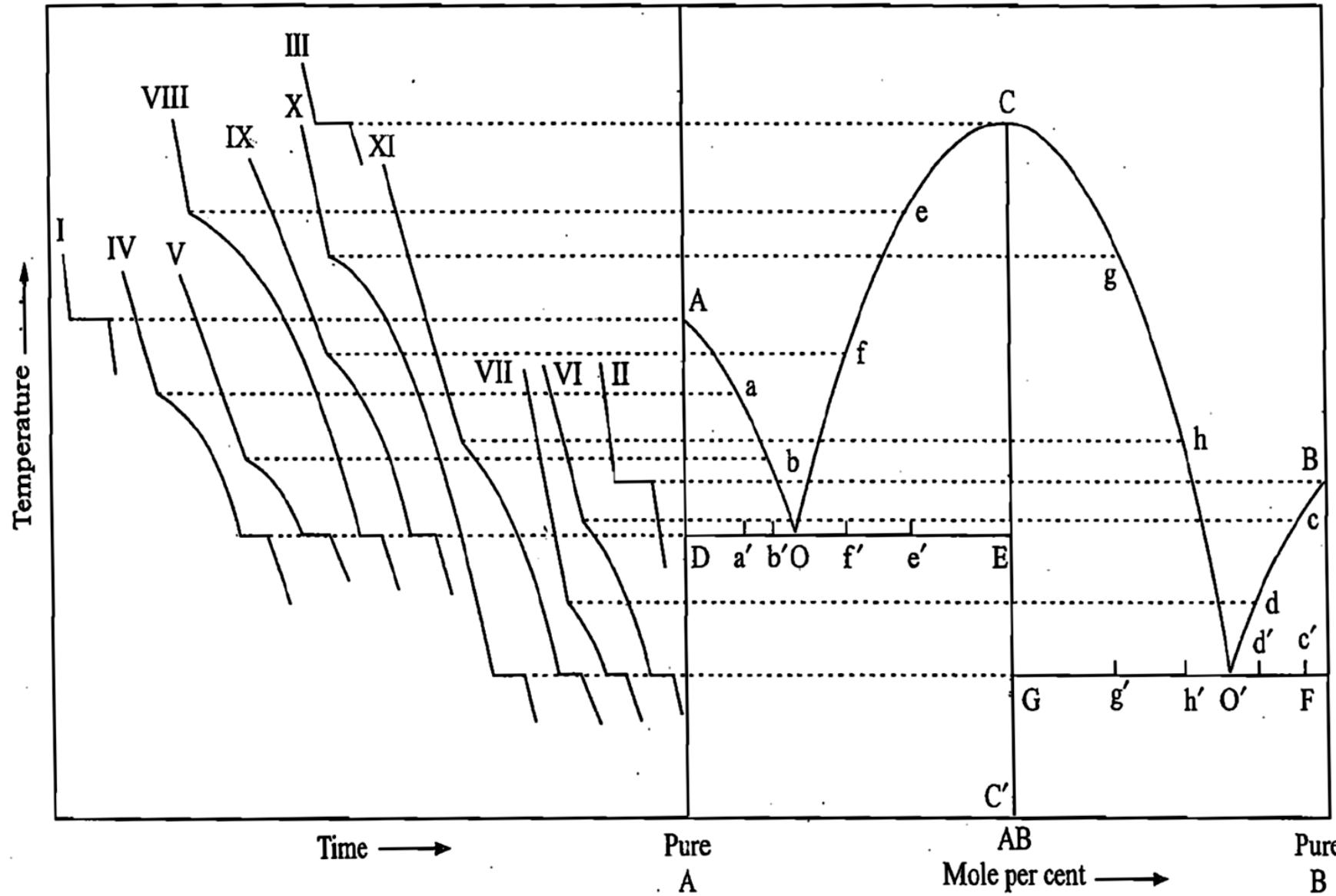


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## Two-component system which forms a stable compound with congruent melting point

- If the two-components of a system at a certain stage enter into chemical combination with one another forming stable compounds, the compound formed may have congruent melting point.
- A compound is said to have **congruent melting point** when it melts sharply at a constant temperature into a liquid of the same composition as that of the solid from which it is derived
- The cooling pattern of the liquid phase of this compound is similar to that of a pure component.



I → Pure A

II → Pure B

IV, V → B in A

VI, VII → A in B

VIII, IX → A in AB

X, XI → B in AB

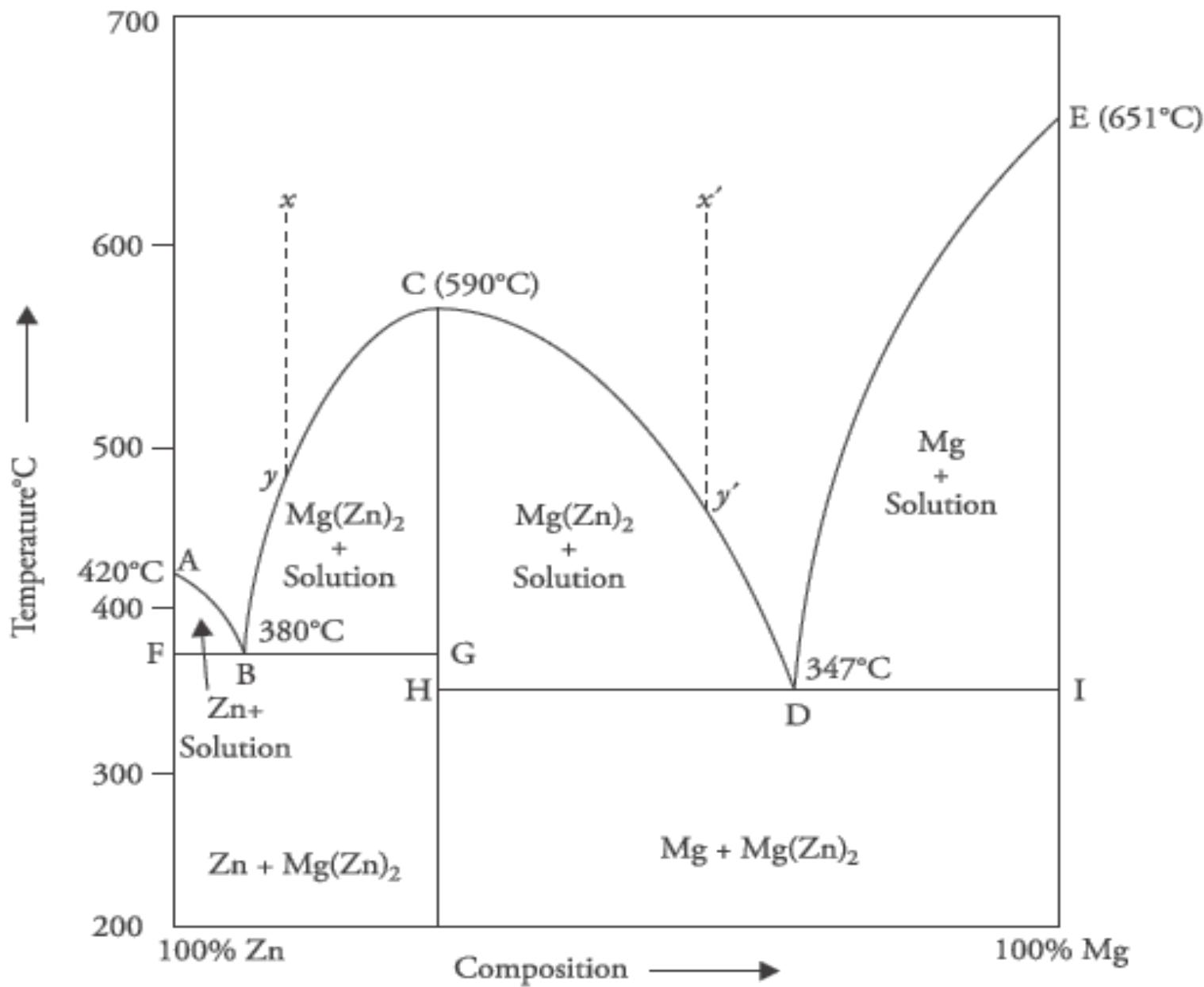
## *Location of the system*

## *Status of the system*

A	Freezing point of A
B	Freezing point of B
C	Freezing point of AB
AO	Freezing point curve of A
BO'	Freezing point curve of B
OC and O'C	Freezing point curves of AB
O	Eutectic point involving solid A, solid AB and liquid O
A-axis	Solid A up to the point A, liquid A beyond A
B-axis	Solid B up to the point B, liquid B beyond B
C'C	Solid AB, liquid AB beyond C
O'	Eutectic point involving solid B, solid AB and liquid O'
DOE	A system on this line represent solid A and solid AB in equilibrium with liquid O
GO'F	A system on this line represents solid B and solid AB in equilibrium with liquid O'
Area AODA	Solid A ⇌ liquid (whose composition lies on AO)
Area BO'FB	Solid B ⇌ liquid (whose composition lies on BO')
Area COEC	Solid AB ⇌ liquid (whose composition lies on OC)
Area CGO'C	Solid AB ⇌ liquid (whose composition lies on CO')
Area below DOE	Solid mixtures of A and AB
Area below GO'F	Solid mixtures of B and AB
Area above AOCO'B	Liquid

# Zinc–Magnesium System

- It is an example of a two-component system in which two metals form a compound having congruent melting point.
- **Compound formed** → Alloy having the formula  $Mg(Zn)_2$  with a melting point of 590 °C, which lies between the melting point of the two metals (The melting point of zinc is 420 °C and that of magnesium is 651 °C)
- $Mg(Zn)_2$  is stable and melts without change in composition
- Experiment is carried out at constant pressure and the vapour phase is not considered → Condensed phase rule will apply
- **Condensed phase rule** →  $F = C - P + 1$



- **POINTS**

**Point A:** Freezing point of zinc ( $420^{\circ}\text{C}$ )

**Point E:** Freezing point of magnesium ( $651^{\circ}\text{C}$ )

**Point C:** Freezing point of  $\text{Mg}(\text{Zn})_2$  ( $590^{\circ}\text{C}$ )

**Point B:** Eutectic point ( $380^{\circ}\text{C}$ ) (Molar composition at B is 79% Zn and 21%  $\text{Mg}(\text{Zn})_2$ )

**Point D:** Eutectic point ( $347^{\circ}\text{C}$ ) (Molar composition at D is 61%  $\text{Mg}(\text{Zn})_2$  and 39% Mg)

- At each of these points, the value of  $C = 1$ ,  $P = 2$  (solid in equilibrium with the liquid of the same composition). Hence,  $F = C - P + 1; 1 - 2 + 1 = 0 \rightarrow$  Invariant System

## CURVES

- **Curve AB**

- ✓ freezing point curve of Zn.
- ✓ On gradual addition of Mg to Zn, the melting point of zinc is lowered along the curve AB.
- ✓ Along this curve, solid zinc is in equilibrium with the solution containing Zn and Mg.

- **Curve ED**

- ✓ Freezing or melting point curve of magnesium on gradual addition of zinc.
  - ✓ Addition of zinc lowers the melting point of magnesium along the curve ED
  - ✓ Along this curve, magnesium is in equilibrium with a solution of Zn and Mg
- ✓ **Applying the condensed phase rule,**  
 $F = C - P + 1 ; 2 - 2 + 1 = 1 \rightarrow$  System is univariant.

- **Curve CB**

- ✓ It represents the lowering of melting point of  $Mg(Zn)_2$  on addition of zinc.
- ✓ System is univariant.

- **Curve CD**

- ✓ It represents the lowering of melting point of  $Mg(Zn)_2$  on addition of magnesium.
- ✓ System is univariant



## AREAS

- **Area ABFA:** Solid zinc in equilibrium with liquid phase whose composition is along AB
  - **Area CBGC:**  $Mg(Zn)_2$  in equilibrium with liquid phase whose composition is along CB
  - **Area CHDC:**  $Mg(Zn)_2$  in equilibrium with liquid phase whose composition is along CD
  - **Area EDIE:** Solid magnesium in equilibrium with liquid phase whose composition is along ED
- ✓ In all above,  $P = 2$ ,  $F = C - P + 1 ; 2 - 2 + 1 = 1 \rightarrow$  **Univariant system**

- **Area below FBG:** A solid mixture of zinc and Mg(Zn)<sub>2</sub>, Hence P = 2.
- **Area below HDI:** A solid mixture of magnesium and Mg(Zn)<sub>2</sub>. Again P = 2.

In the above, F = C – P + 1 ; 2 – 2 + 1 = 1 → **Univariant System**

- **Area above ABCDE:** It represents a single phase consisting of molten zinc and magnesium.

→ P = 1; C = 2 F = C – P + 1 ; 2 – 1 + 1 = 2 → **The system is bivariant**

- **EUTECTIC POINTS**

- **Point B:**

- ✓ The three phases, zinc, Mg (Zn)<sub>2</sub> and their melt are in equilibrium
- ✓ The eutectic temperature at B is 380 °C and the composition is 79% Zn and 21% Mg (Zn)<sub>2</sub>

- **Point C:**

- ✓ The three phases, magnesium, Mg (Zn)<sub>2</sub> and melt are in equilibrium.
- ✓ The eutectic temperature at D is 347 °C and the composition is 61% Mg(Zn)<sub>2</sub> and 39% Mg.

→ C = 2; P = 3 ; F = C – P + 1 = 2 – 3 + 1 = 0 **The system is invariant.**

## • Conclusion

- The phase diagram of the Zn–Mg system can be considered to be made up of two simple eutectic diagrams side by side, one on the left of CG and the other on its right
- The rounded maxima (Point C) indicates that the compound formed is not very stable and dissociates partly. The dissociation of products in the liquid phase depresses the actual melting point of the compound resulting in a rounded melting point.

# THANK YOU



# APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 7



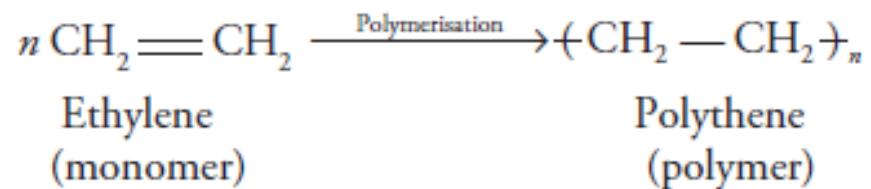
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# POLYMERS

- Polymers are compounds of very high molecular weights formed by the combination of a large number of small repeating units.  


MONOMER
  - The process by which the simple molecules (monomers) are converted into polymers is called polymerization



$n \rightarrow$  Degree of Polymerization

- Difference between polymer and macromolecule:
    - A polymer contains repeating units (monomers), whereas a macromolecule is a giant molecule that may or may not contain monomer units.
    - All polymers are macromolecules and not *vice versa*.
    - Chlorophyll and haemoglobin are macromolecules but not polymers. Polyethene may be regarded as a polymer as well as a macromolecule

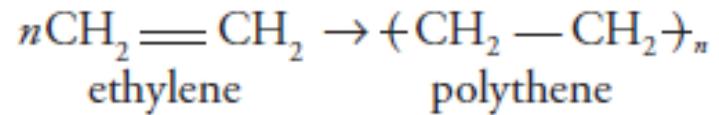
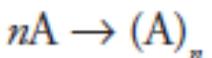
# Classification of Polymers

## **1. On the basis of origin.**

- **Natural polymers** They are polymers that occur in nature. For example, starch (polymer of  $\alpha$ -D-glucose), cellulose (a polymer of  $\beta$ -D-glucose), proteins (polymer of  $\alpha$ -amino acids)
  - **Synthetic polymer** It is a polymer that is prepared artificially in the laboratory. For example, polyethylene (PE), polyvinylchloride (PVC), nylon

## 2. On the basis of monomer composition

- **Homopolymer** If a polymer consists of identical monomers, it is termed as homopolymer.



- **Copolymer** If a polymer is made up of more than one type of monomers it is called a copolymer.



- Depending on the arrangement of the monomeric units, the copolymers may be further classified as:

✓ **Random copolymers** The monomeric units are randomly arranged.



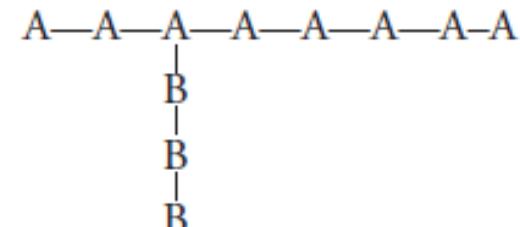
✓ **Alternating copolymers** The monomeric units are arranged in an alternating manner



✓ **Block copolymers** The monomeric units are arranged in blocks.



✓ **Graft copolymers** They are branched copolymers in which the backbone is formed of one type of monomer and the branches are formed of the other types of monomers



### 3. On the basis of chain structure

- **Linear polymer** → It has no branching other than the pendant groups associated with the monomer.
  - well packed and therefore have high densities. For example, polythene, nylons
- **Branched Polymer:** → polymers in which the monomers are joined to form long chains with side chains
  - irregularly packed and have low densities.
  - If the side chain is different from parent chain, they are called graft polymers.
  - For example, low-density polyethene, glycogen,
- **Cross-linked polymers/ Network polymers** → monomer units are linked together to form a three-dimensional network.
  - hard, rigid and brittle. For example, bakelite, vulcanised rubber

## 4. Based on chain composition

- **Homochain polymer** Polymers having all carbon atoms along their backbone. For example, polyethene, PVC, rubber, etc.
- **Heterochain polymer** If the polymeric chain contains a heteroatom. For example, nylon (polymeric chain contains nitrogen atom) and terylene (polymeric chain contains oxygen atom).

## 5. Based on polymerisation mechanism

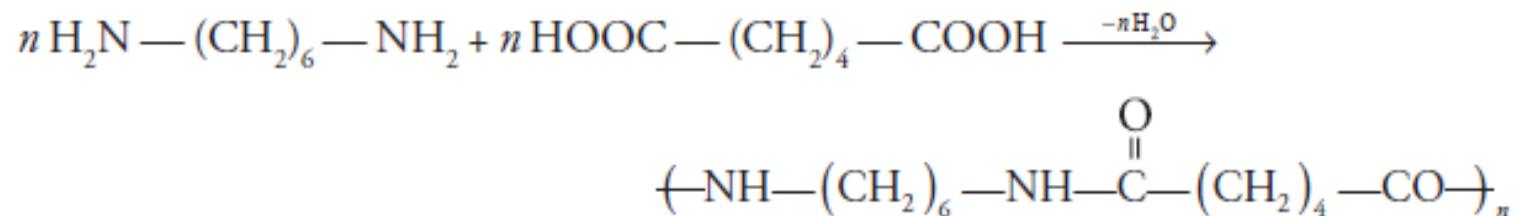
- **Addition polymers** → Those polymers that are obtained by the addition of monomeric units are called addition polymers. Example, polyethene, PVC,  
→ The molecular weight of such a polymer is an exact multiple of the molecular weight of the monomer.



$$\text{Molecular weight of polymer} = n \times \text{molecular weight of monomer.}$$

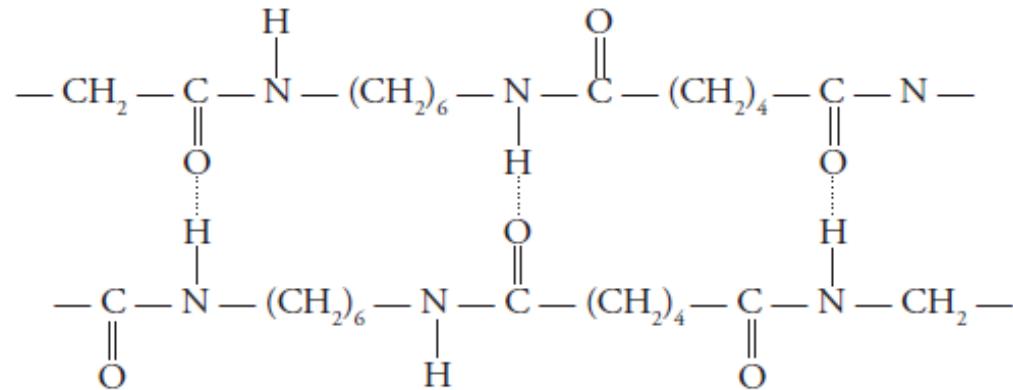
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- **Condensation polymers** → A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia and hydrochloric acid
- The molecular weight of such a polymer is not an exact multiple of the molecular weight of the monomer.
- Example: Nylon 6,6 is obtained by the condensation of two monomers, hexamethylenediamine and adipic acid with the loss of water molecules.



## 6. Based on molecular forces

- **Elastomers:** They are polymers held by weakest intermolecular forces and have elastic behavior. For example, natural rubber.
- **Fibres:** These are polymers whose polymeric chains are held together by strong intermolecular forces like hydrogen bonds or dipole–dipole interactions. For example, nylon 6,6, polyester, silk

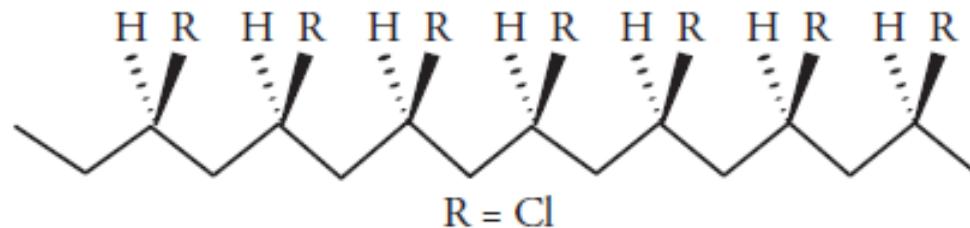


*Hydrogen bonding in Nylon 66*

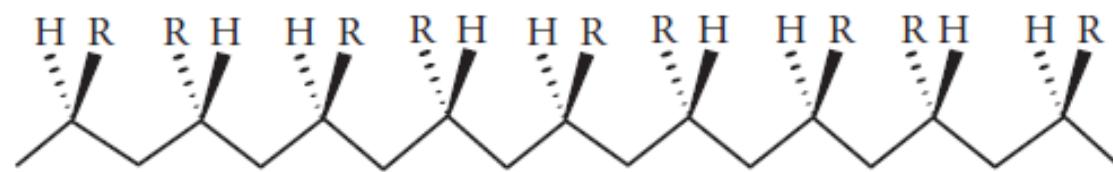
- **Thermoplastics** → They are linear, long-chain polymers that soften on heating and harden when cooled.  
 → The intermolecular forces of these polymers are intermediate between those of elastomers and fibres  
 → There is no cross-linking between the polymeric chains. Eg. polyethene (PE), polystyrene, PVC, teflon,
- **Thermosetting plastics** → They are polymers that can change irreversibly into hard and rigid materials on heating and cannot be reshaped once they set.  
 → They form hard, infusible, insoluble products because of cross-linkages. For example, bakelite, melamine

**7. Based on tacticity :** Tacticity is defined as the spatial arrangement of the substituent groups on the asymmetric carbon atom.

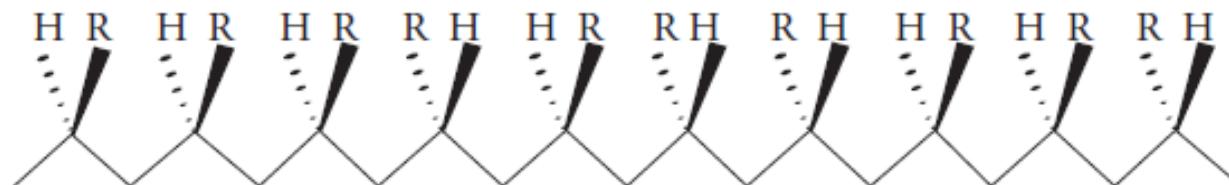
- **Isotactic polymers** When the orientation of side groups (R) on all asymmetric carbon atoms is the same



- **Syndiotactic polymer** When the orientation of the side groups on alternate asymmetric carbon atoms is the same,



- **Atactic polymer** When the side groups have no preferential arrangement and are randomly arranged,



## 8. Based on degree of polymerisation

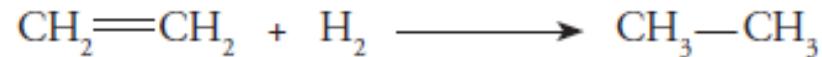
- **Oligopolymers:** Polymers with low degree of polymerisation are called ‘oligopolymers’.
- **Macromolecules:** Polymers with a high degree of polymerisation are called ‘high polymers’. They have very high molecular weights ( $10^4$ – $10^6$ ) and hence are called macromolecules.

## 9. Based on chemical composition

- **Organic polymers:** A polymer whose backbone chain is made mainly of carbon atoms and the side chains consist of oxygen, nitrogen, sulphur, etc. Examples include polythene, PVC, nylon, etc.
- **Inorganic polymers:** These polymers do not have a carbon backbone chain. Examples include silicone rubbers, phosphazene

# Functionality

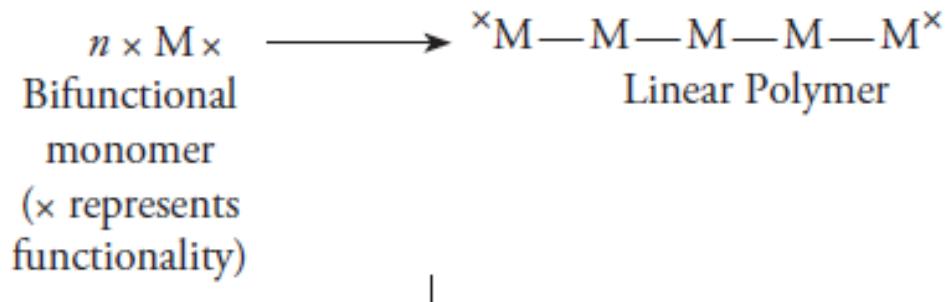
- The number of reactive sites in a molecule is termed as its functionality.
- For a molecule to act as a monomer it must have at least two reactive sites, that is, its functionality should be two.
- Ethylene can add two atoms of hydrogen or halogen. → **Bifunctional**



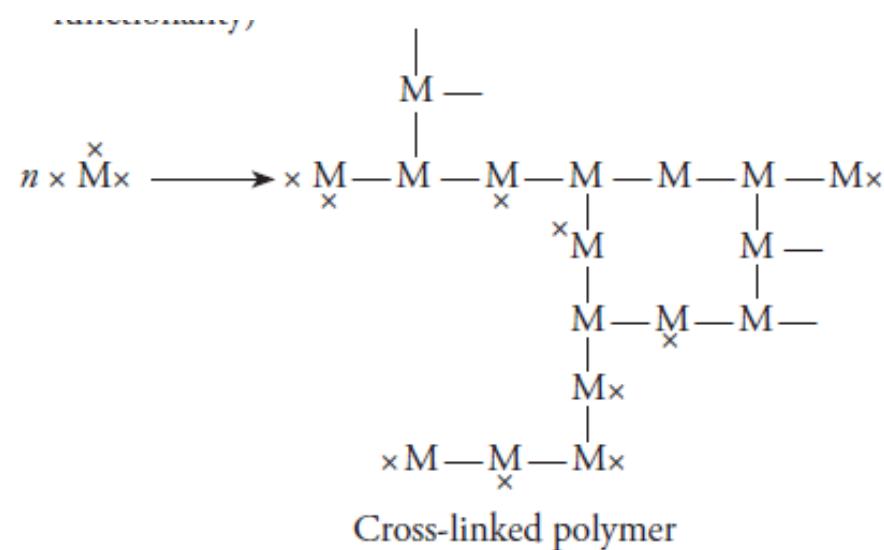
- Acetylene has a functionality of four (**tetrafunctional**), as it can react with four atoms of hydrogen or halogen.



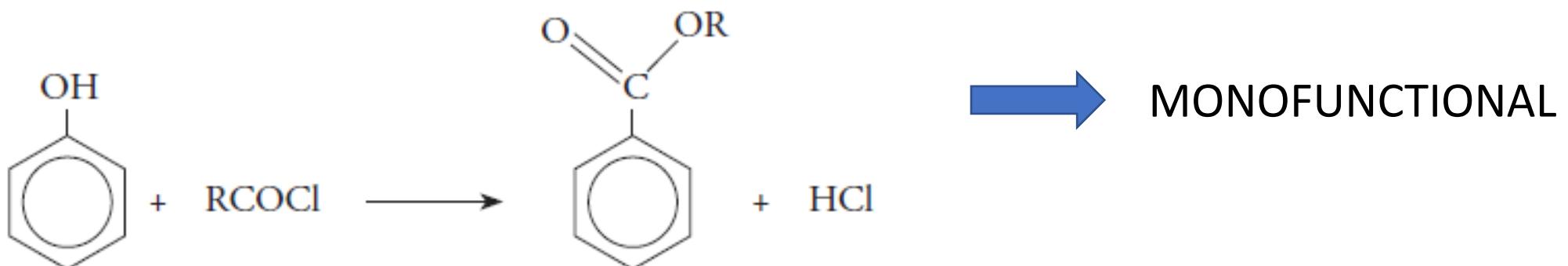
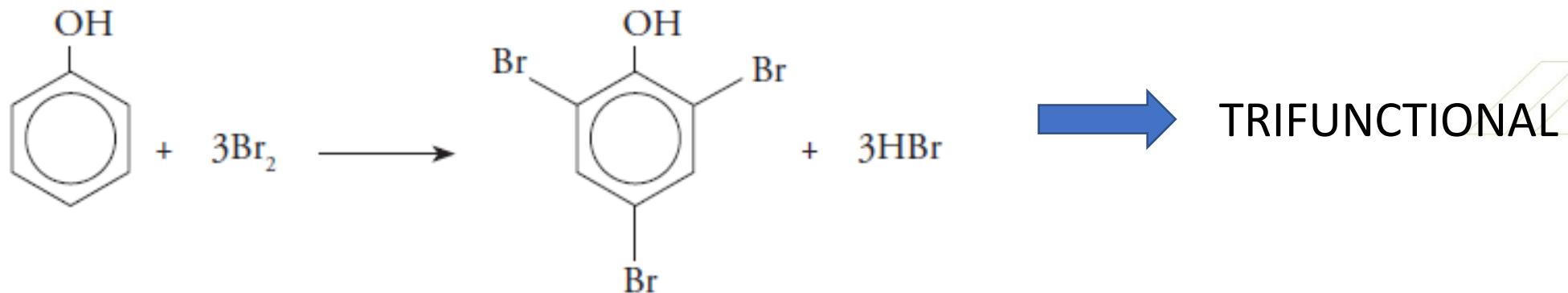
- Bifunctional monomer (ethylene, propylene, vinyl chloride, styrene, etc.) → a linear polymer is formed.



- A trifunctional monomer → formation of a cross-linked polymer,

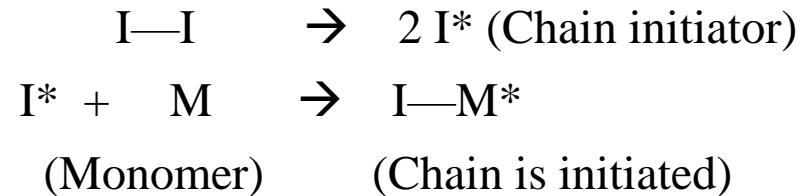


- Phenol can be trifunctional or monofunctional depending on the functionality used

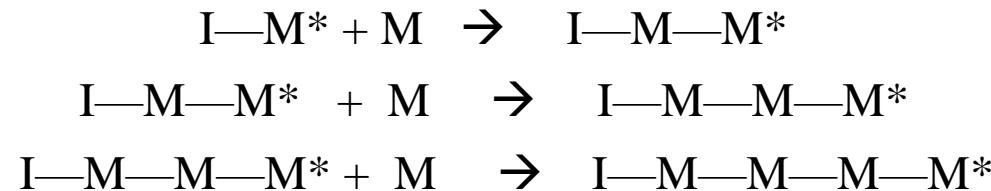


# Addition Polymerization

- Addition polymerisation consists of three important steps
- Step I : **Chain initiation** → This step involves the formation of active molecules called chain initiators.  
→ These chain initiators then attack the monomer to initiate the chain formation.



- Step II: **Chain propagation** The initiated chain then attacks more monomeric molecules leading to the increase in the length of the chain.



- Step 3: **Chain termination** The active centers are removed or they combine with each other and the chain propagation comes to an end.

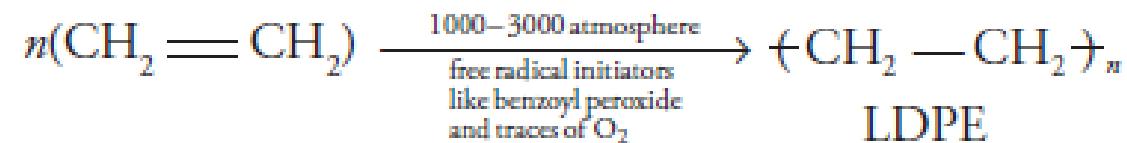


# Polyethylene – Addition Polymer

- Polyethene is an important thermoplastic resin prepared by the addition polymerisation of ethylene.
- **TYPES**

## 1. Low-density polyethylene

- **Preparation** It is prepared by the polymerisation of ethylene at high pressure (1000–3000 atmospheres) at 250 °C in the presence of free radical initiators like benzoyl peroxide. Traces of oxygen catalyse the reaction.



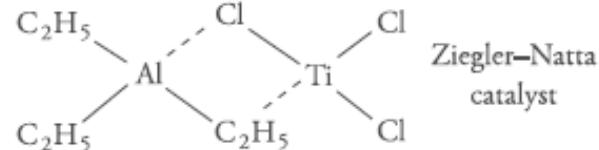
**Properties :** → It is a waxy solid that floats on water and has a linear branched structure.

- The branches do not allow the chains to pack efficiently; hence, its density is low (0.91–0.925 g/cm<sup>3</sup>).
- It is not polar and has weak intermolecular forces.
- It is tough, flexible, chemically inert and has excellent electrical insulation properties.

- **Applications:** Used for storing a variety of foodstuffs. It is used for making carrier bags, films for general packing, moulded toys, mugs and ink tubes for pens.

## 2. High-density polyethylene

- **Preparation**
- Ethylene is polymerised under 6–8 atmospheric pressure at 60–70 °C in the presence of Ziegler–Natta catalyst (triethylaluminium and titanium tetrachloride).



OR

- At 35 atmospheric pressure, 60–200 °C temperature and in the presence of metal oxide catalyst like CrO<sub>3</sub> supported on silica alumina, ethylene polymerises to give high-density polyethene (HDPE).
- **Properties:** → The polymeric chains are linear and hence they pack easily. Hence, it has high density (0.95–0.97 g/cm<sup>3</sup>).  
→ It is more stiff, hard and has greater tensile strength compared with LDPE.  
→ Its softening temperature is high (135 °C). It has excellent electrical insulation properties, has low water and gas permeability, has excellent chemical resistance and is free from odor and toxicity.

### • Applications

- It is used for making insulations, pipes, bottles for milk, household chemicals and drug packing.
- It is also used for the manufacture of crates, industrial containers and overhead tanks.

### **3. Linear low-density polyethylene (LLDPE)**

- **Preparation :** It is made by copolymerizing ethylene and 1–butene (with lesser amounts of 1-hexene and higher 1-alkenes to vary the density) using Ziegler-type catalysts.
- **Properties →** The resultant structure has a linear backbone, but it has short, uniform branches that, like the longer branches of LDPE, prevent the polymer chains from packing closely together.
  - LLDPE is attractive because it requires considerably less energy to produce than LDPE and that the polymer's properties may be altered by varying the type and amount of its chemical ingredients.
  - density between about 0.915 and 0.930 g/cm<sup>3</sup>
  - The higher tensile strength, superior impact and puncture resistance than LDPE
- **Applications:** It is used in making golf ball covers, orthopaedic devices, blending with LDPE, packing films and bottles.

## 4. UHMWPE (ultrahigh molecular-weight polyethylene)

**Preparation :** Polymerization of ethylene using Ziegler-Natta catalysts OR Fujita's catalysts OR metallocene catalysts

Ziegler Nata Catalyst → To prepare or obtain Ziegler-Natta catalysts, transition metal halides belonging to groups IV-VIII are generally reacted with organometallic compounds that belong to groups I – III in the modern periodic table. One common example is a mixture of titanium tetrachloride ( $TiCl_4$ ) and trimethylaluminum ( $Al(C_2H_5)_3$ ).

Fujita's catalyst → Catalysts with transition metals as catalytic centers and bis[phenoxy-imine] as ligands



- **Properties:** → It has extremely long chains, with a molecular mass usually between 3.5 and 7.5 million amu
  - The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. This results in a very tough material.
  - excellent resistance to low temperature, good chemical stability, and low solubility at room temperature.
  - UHMWPE molecules typically having 100,000 to 250,000 monomer units per molecule each compared to HDPE's 700 to 1,800 monomers.
- **Applications:** It is used in making surgical prostheses, machine parts, heavy-duty liners.

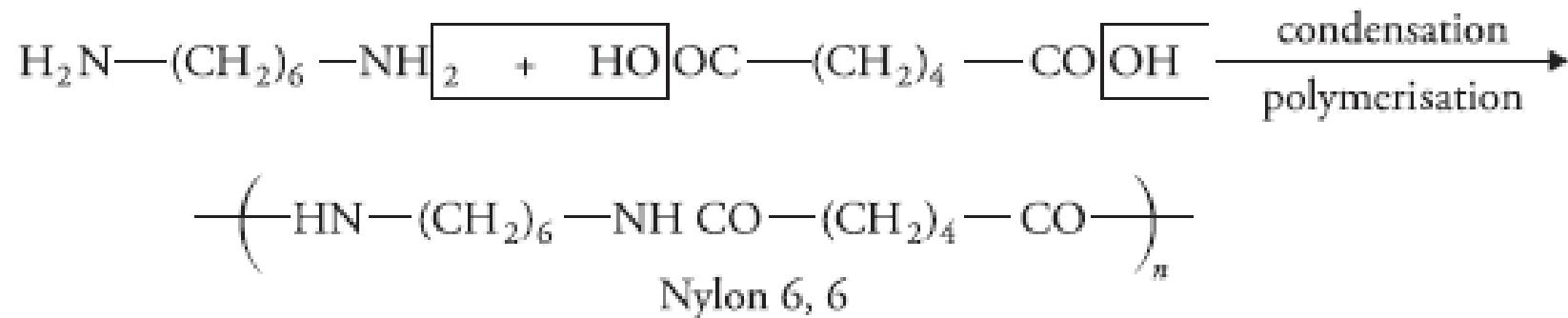
# Condensation polymers

- In condensation polymerisation, the polymerisation reaction proceeds step by step through reaction between the functional groups of the monomers with the removal of small molecules like water.

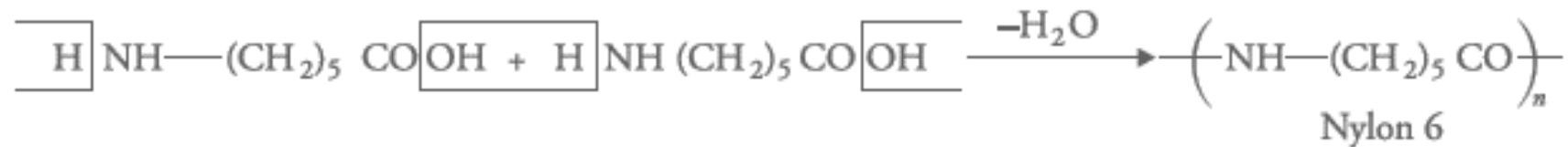
## 1. NYLONS

### ➤ NYLON 6,6

→ They are polyamide polymers having recurring amide groups. Nylon 6, 6 is formed by the condensation of hexamethylenediamine and adipic acid.

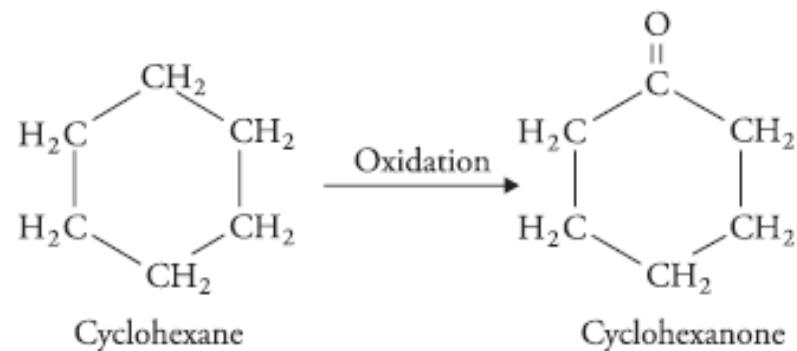


➤ **NYLON 6 :** It is produced by the self-condensation of *e* -aminocaproic acid.

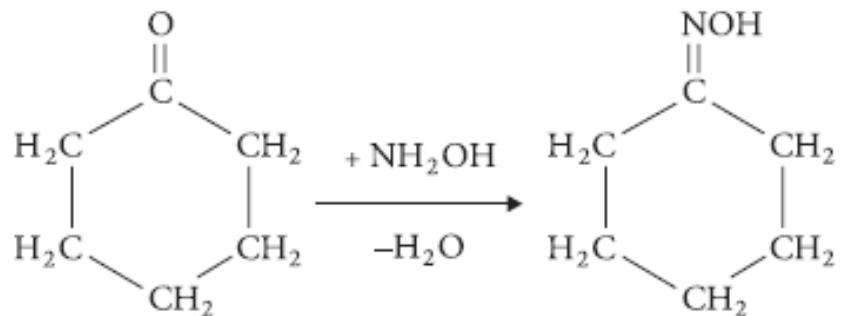


## → Steps for the synthesis of nylon-6

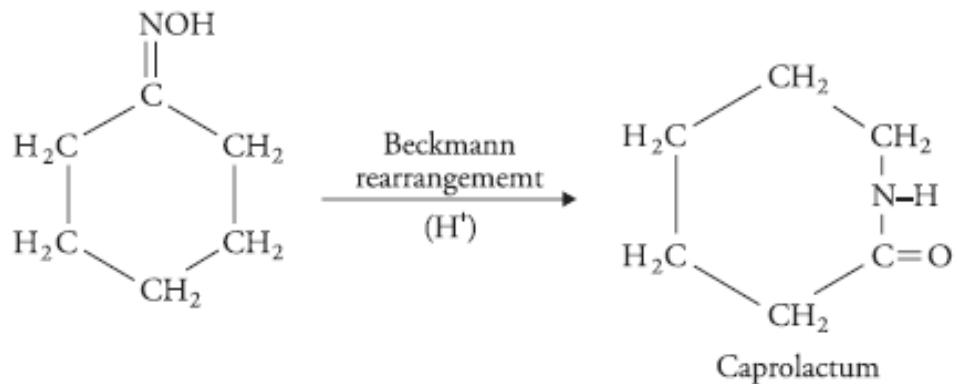
### **Step (i) Conversion of cyclohexane to cyclohexanone by oxidation.**



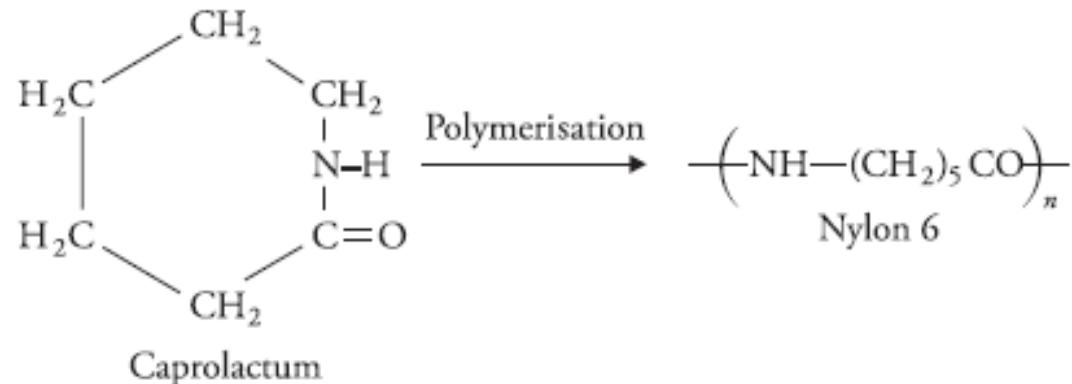
**Step (ii)** Cyclohexanone reacts with hydroxylamine  $\text{NH}_2\text{OH}$  to form cyclohexanone-oxime.



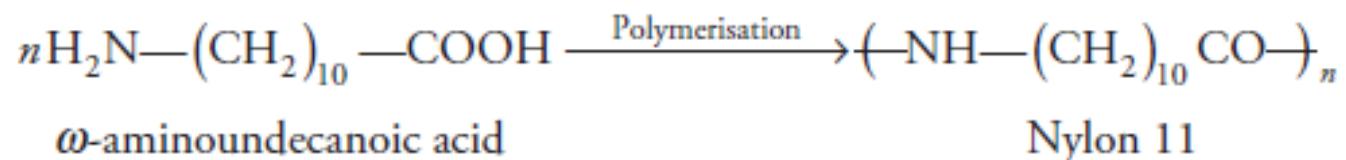
**Step (iii)** Conversion of cyclohexanone-oxime into caprolactum by Beckmann rearrangement in the presence of  $\text{H}_2\text{SO}_4$ .



- **Step (iv)** Ring opening and polymerisation of caprolactum to give nylon-6.



➤ **NYLON 11** → It is prepared by the self-condensation of *w* -aminoundecanoic acid.

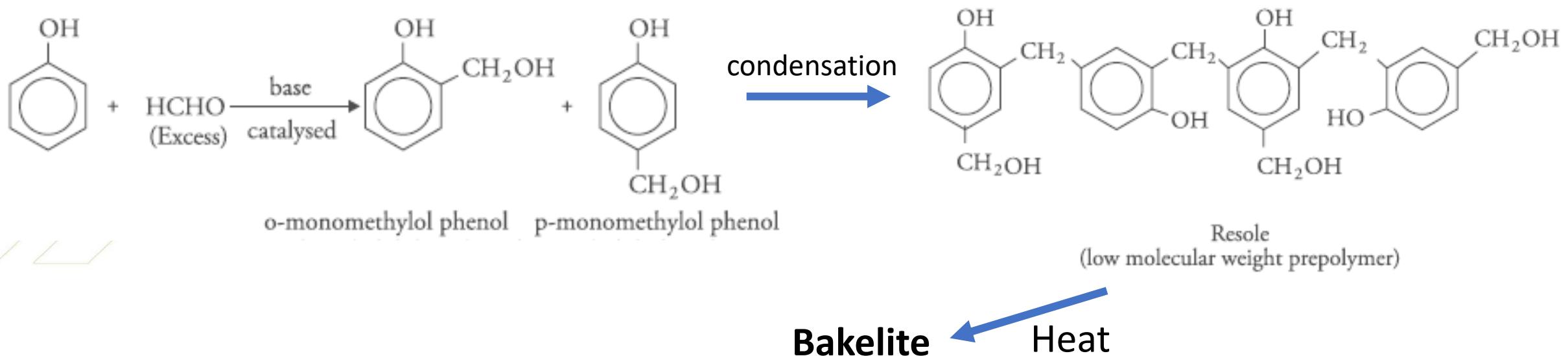


- **Properties of Nylons:** → It is a linear polymer. The polymeric chains are held together by hydrogen bonding.  
→ They are translucent, high-melting polymers known for their toughness, abrasion resistance, elasticity and high crystallinity.
- **Applications:** → Nylon 6,6 is used for making fibres that are used for making socks, carpets, etc.  
→ It also finds use in mechanical engineering for the manufacture of gears, bearings, bushes, electrical mountings. Nylon moving parts work quietly without any lubrication.  
→ Nylon 6 is mainly used for making tyre cords.  
→ Bristles, brushes are generally made of Nylon 6, 10. Nylon 11  
→ Glass-reinforced nylon plastics find use in domestic appliances, radiator parts of cars, etc.

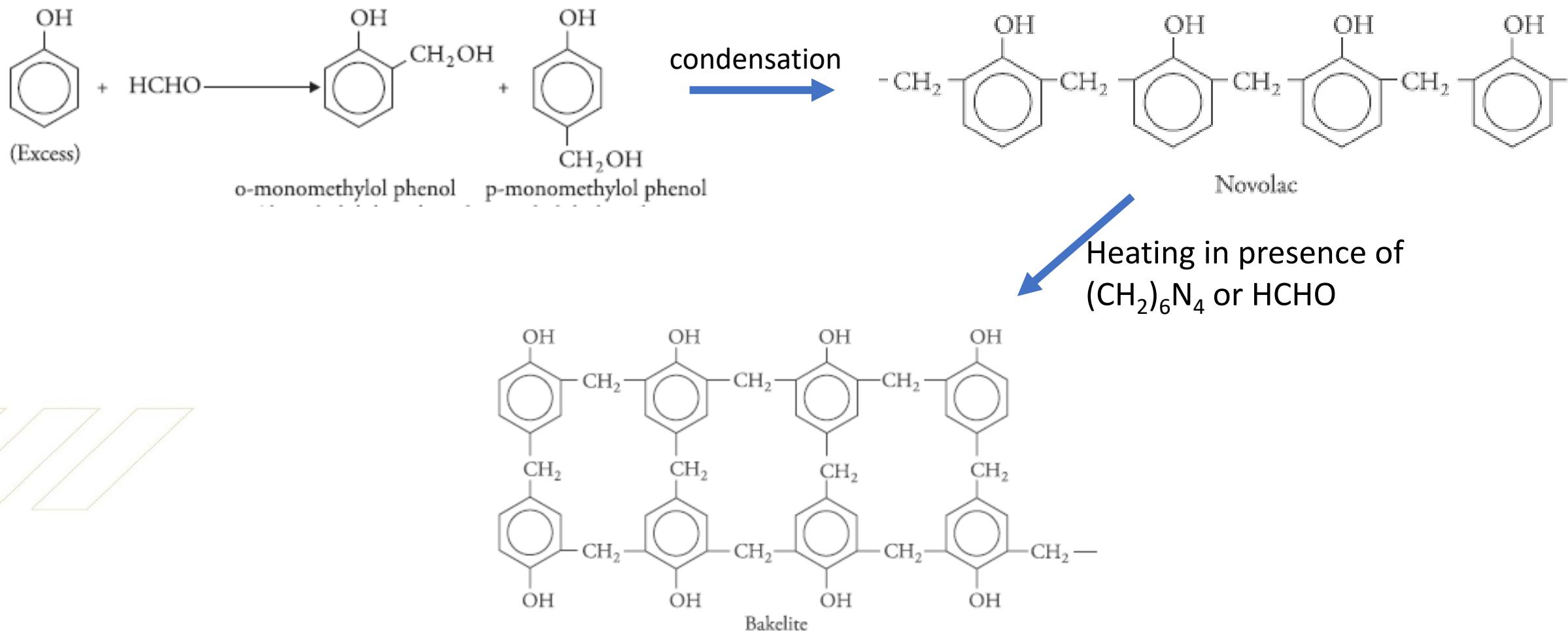
## 2. Bakelite (Phenol formaldehyde resin)/ Phenoplasts/ PF resins

- **Preparation:** 2 different methods are used.

→ **I method:** Base catalysed using excess of formaldehyde over phenol. The initially formed product called ‘resole’ changes into thermosetting polymer ‘bakelite’ simply by heating.



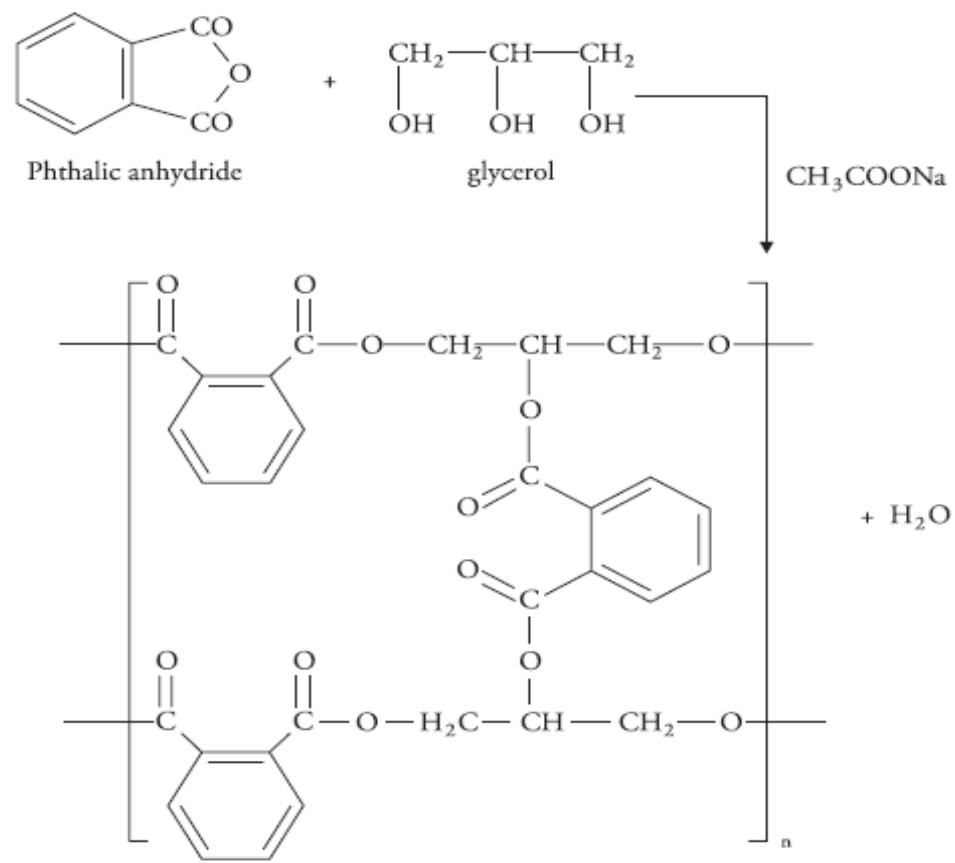
- **Method II:** Acid catalysed method using excess of phenol.



- **Properties →** Phenolic resins are hard, rigid, strong with excellent heat, moisture, chemical and abrasion-resistance.  
→ They are scratch-resistant and possess excellent electrical insulating properties.
- **Applications:** → They are used for making domestic switches, plugs, handles for pressure cookers, saucepans and frypans.  
→ They are also used for making moulded articles like telephone parts, cabinets for radio and television.  
→ They find use as adhesives for grinding wheels and brake linings.  
→ They are used in paints and varnishes, in the production of ion-exchange resins for water-softening and for making bearings used in propeller shafts for paper industry and rolling mills.

### 3. Glyptal

- Preparation: Glyptal is a cross-linked, thermoset polyester. It is prepared by condensing glycerol (a triol) with phthalic anhydride



Glyptal

- **Properties:** → Glyptal is harder and more brittle than the linear polyesters. It does not soften when heated. The cross-linking keeps the polymer chains from moving with respect to one another when heated.
  - It is a fast drying thermoplastic that can bond a variety of materials.
  - It has strong, durable bonds that have excellent resistance to oil, gasoline and moisture.
- **Uses:** → Glyptal are useful as coating materials and are not used for making fibres and plastic products.
  - Glyptal was first commercialised in 1902 for use in paints and varnish industry. Glyptal is added in paints to improve their washability and adhesion.
  - Its fast drying time along with its good dielectric strength makes it an excellent general-purpose adhesive for many electrical and non-electrical applications.
  - It is also used as a sealing wax.

# THANK YOU



# APPLIED CHEMISTRY

Paper Code: BS103/ BS104

Lecture 7



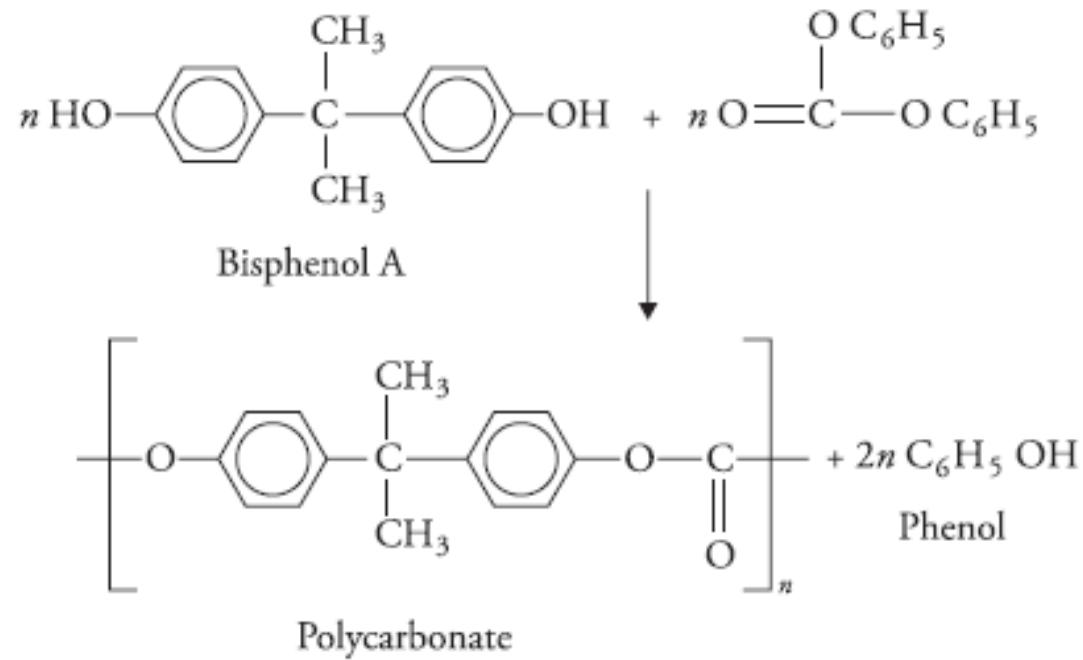
SCHOOL OF  
ENGINEERING AND  
TECHNOLOGY



# Speciality Polymers

## 1. Engineering thermoplastics-Polycarbonate

- **Preparation:** → They can be prepared by the condensation of diphenoxymethylene derivatives with diphenyl carbonate.
- 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A) on reaction with diphenyl carbonate gives polycarbonate.



## Properties

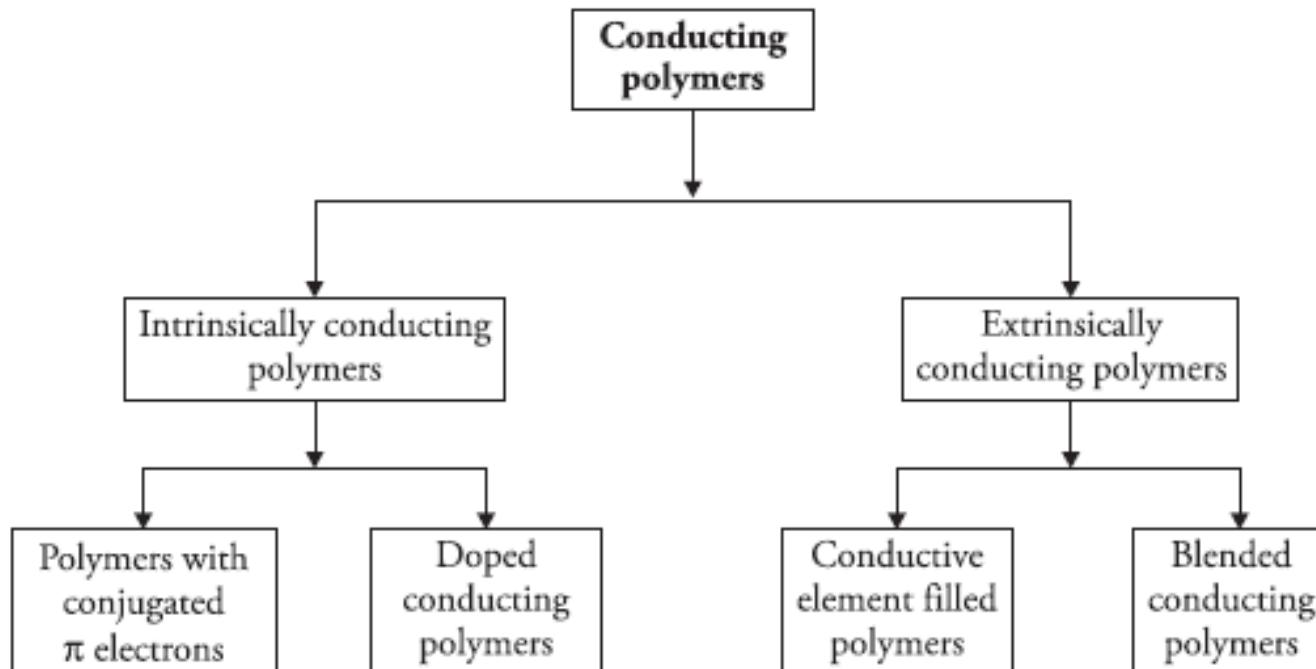
- It is **tough, strong, generally transparent, amorphous solid with outstanding impact resistance.**
- It maintains its shape and size even under great stress over a wide range of temperature.
- It is **resistant to water, acids, detergents, oils and greases**, but is attacked by bases, halogenated solvents, ketones organic solvents like benzene, benzylalcohol, dimethyl ether, carbondisulphide, etc.
- It has **excellent resistance to high temperatures upto 140 °C** and maintains toughness at low temperatures upto **-20 °C.**
- It **has good electrical insulation properties.**

**Applications:** → Owing to its electrical properties and dimensional stability, it is used for mouldings for computers, calculating machines, for making hair driers, electric razors, CDs and DVDs.

- Owing to its excellent impact resistance, it is used in automobile industry for making motorcycle windshields, police shields, headlight covers, car bumpers, front panels, safety helmets, etc.
- As it is not stained by oils, greases and domestic beverages, it is used for making blenders, food processing bowls, coffee maker, food mixer housings.
- Owing to its temperature resistance, stability and chemical inertness, it finds use in the manufacture of baby bottles, syringes.

## 2. Conducting Polymers

Polymers that conduct electricity are called conducting polymers. They can be classified as follows.



## 1. Intrinsically conducting polymers

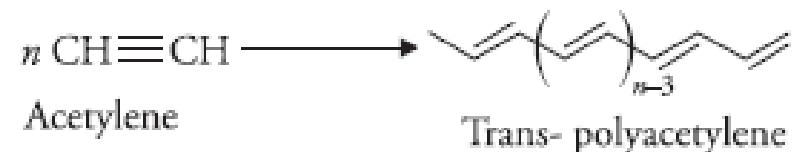
- The conductance of these polymers is due to the extensive conjugation in their backbone. They are further of two types:

### a. Conjugated $\pi$ -electron conducting polymers

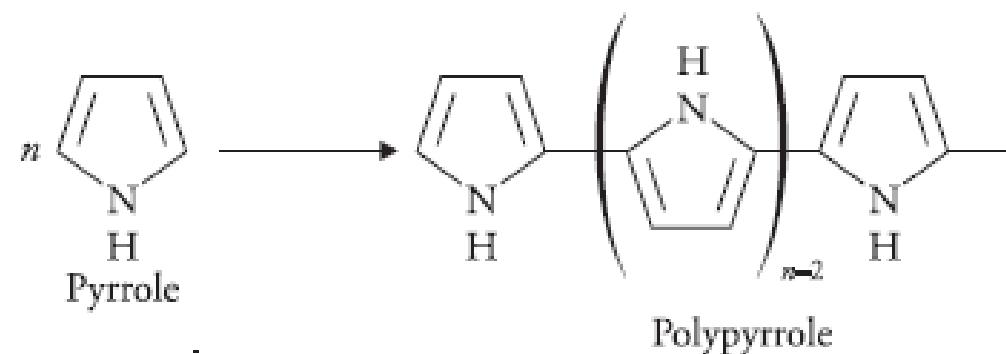
→ The conductivity of these polymers is due to the presence of conjugated  $\pi$  -electrons. The conjugated  $\pi$  electrons are delocalised.

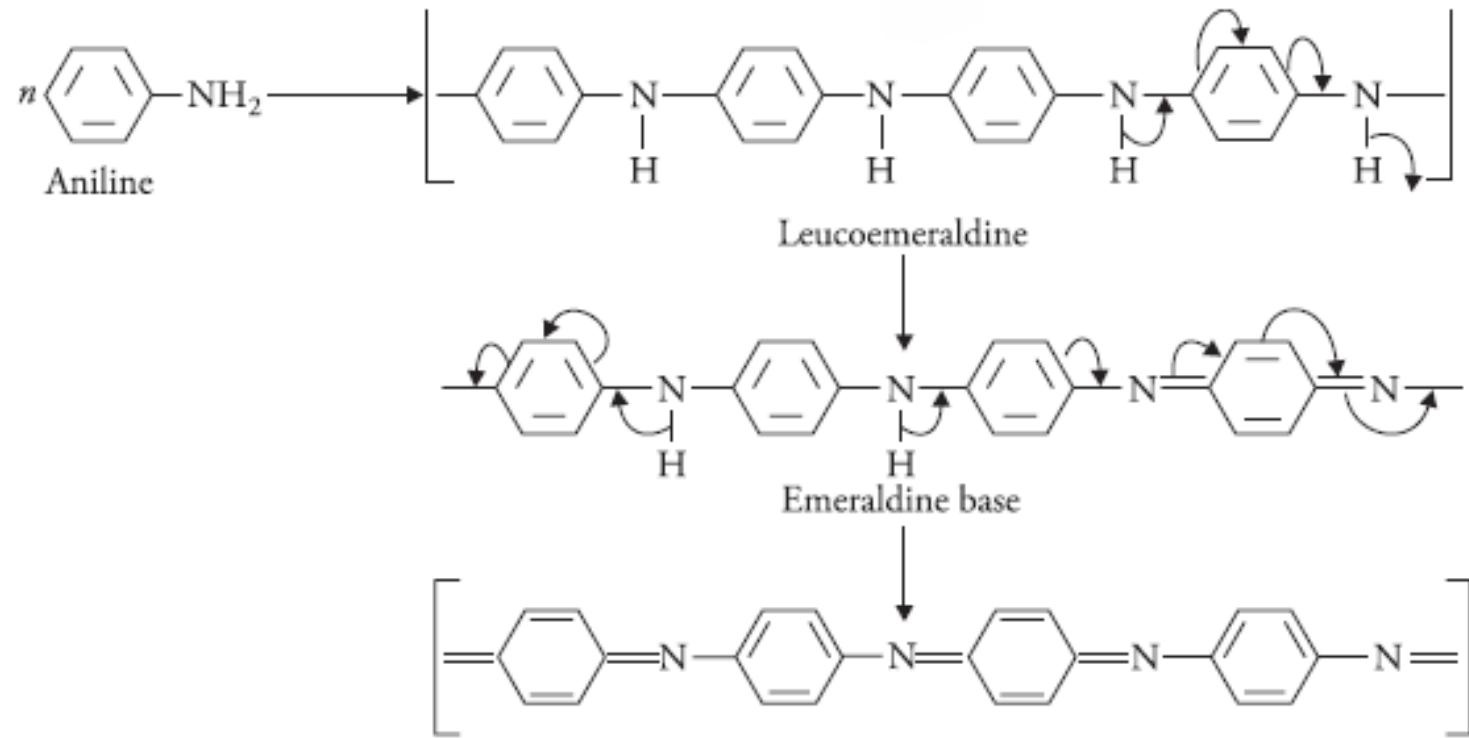
→ In an electric field, the  $\pi$  electrons get excited and are transported through the solid polymeric material.

→ Examples:



→ The conductivity of polyacetylene is  $1.7 \times 10^{-9} \text{ S cm}^{-1}$





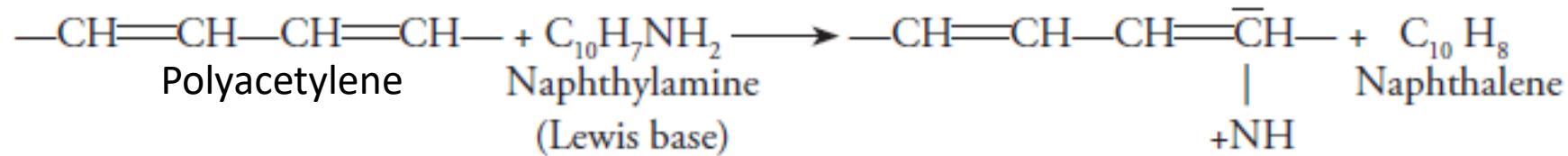
→ All the three forms of aniline conduct electricity. Conductivity of polyaniline is  $10^{-10} \text{ S cm}^{-1}$ .

**b. Doped conducting polymers** The polymers are doped by adding either electron donors or electron acceptors on the polymeric backbone. Doping can be of two types:

➤ **p-type doping** When the polymer is treated with a lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used p dopants are  $I_2$ ,  $FeCl_3$ ,  $Br_2$ ,  $AsF_5$ , etc. For example,



➤ **n-type doping** When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na, naphthylamine, etc. For example,



- The conductivity of the above polymers depends on various factors.:  
 (i) **Length of conjugation of the polymeric chain** Greater the conjugation level, more will be the delocalised electrons and greater will be the conductivity.  
 (ii) **Doping level** Conductivity increases with the increase in the amount of dopant.  
 (iii) **Temperature** Contrary to metals, the conductivity of these polymers increases with the rise in temperature.

**2. Extrinsically conducting polymers:** The conductivity of these polymers is due to presence of externally added ingredients. They are of two types.

i. **Conductive element-filled polymers** → When the polymer is filled with conducting elements like carbon black, metallic fibres, metal oxides, their conductivity rises.

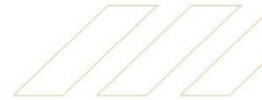
→ Here the polymer acts as the binder of the conducting elements. However, addition of these elements affects tensile strength and impact strength of the polymer.

→ This problem is overcome by blending a conventional polymer with a conducting polymer.

ii. **Blended conducting polymer:** Conducting polymers are added to conventional polymers. The blended polymers have better physical, chemical and mechanical properties.

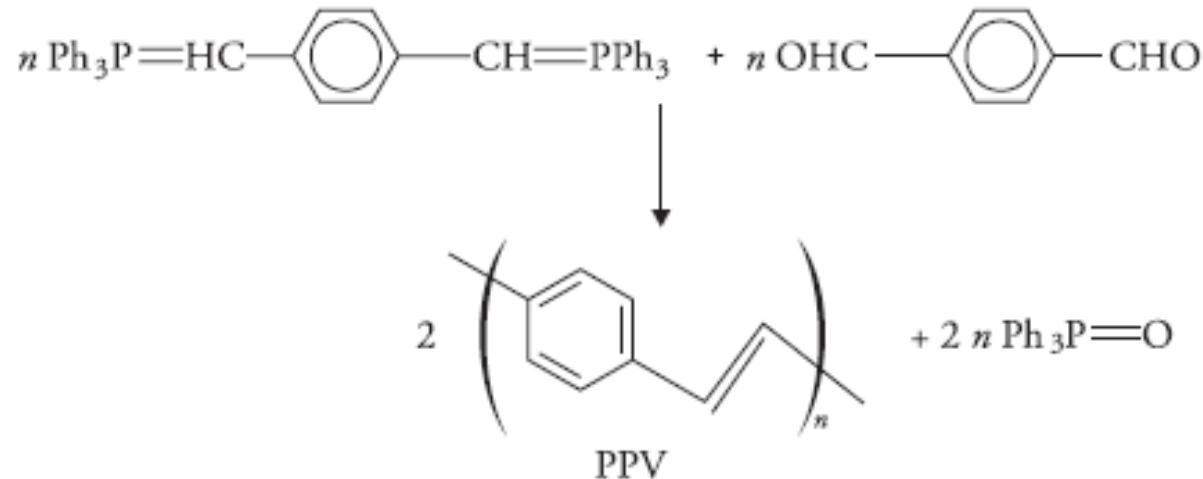
## • Applications of conducting polymers

- In rechargeable light weight batteries. These have perchlorate-doped polyacetylene-lithium system. These batteries are light in weight, leak-proof and small in size.
- Used in photovoltaic devices like in Al/polymer/Au photovoltaic cells.
- In telecommunication systems.
- Electrically conducting polyaniline is used for antistatic coatings, and also for producing ‘smart windows’. Polyaniline shows different colors in different oxidation states. Hence, its color changes in response to sunlight or temperature changes.
- They are also used in organic light-emitting diodes (OLEDs).
- In electronic devices such as transistors and diodes.



### 3. Electroluminescent Polymers

- Electroluminescence is light emission stimulated by electric current
  - The phenomenon is particularly useful as enough power can be put through the device at low voltages to generate practical amounts of light.
  - An OLED is made of sheets of polymer semiconductor material resembling plastic.
  - Polymer LEDs were first discovered in 1989 by Richard Friend and co-workers at Cambridge University using polyphenylene vinylene (PPV) as the emissive layer.
- **Preparation:** PPV can be synthesised by Wittig-type coupling between bis (ylide) derived from an aromatic bisphosphonium salt and dialdehyde, especially 1, 4-benzenedialdehyde.



## Properties

- PPV is a bright yellow, fluorescent polymer.
- It is insoluble, intractable and infusible. Incorporation of side groups like alkyl, alkoxy or phenyl increases the solubility of the polymer.
- It is a diamagnetic material with low intrinsic electrical conductivity (of the order of  $10^{-13} \text{ S cm}^{-1}$ ). The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals or acids. However, the stability of these doped materials is low.
- Alkoxy-substituted PPVs are easier to oxidise than the parent PPV and hence have much higher conductivities.

- **Applications**

- As PPV is capable of electroluminescence, it is used in polymer-based OLEDs.
- Devices based on PPV emit yellow green light.
- Derivatives obtained by substitution of PPV are used when light of a different color is desired.
- PPV is also used as an electron-donating material in organic solar cells.



- **Limitations of PPV**

- It is susceptible to photodegradation and oxidative degradation in the presence of oxygen. Hence, precautions are to be taken to prevent oxygen contamination during manufacturing.

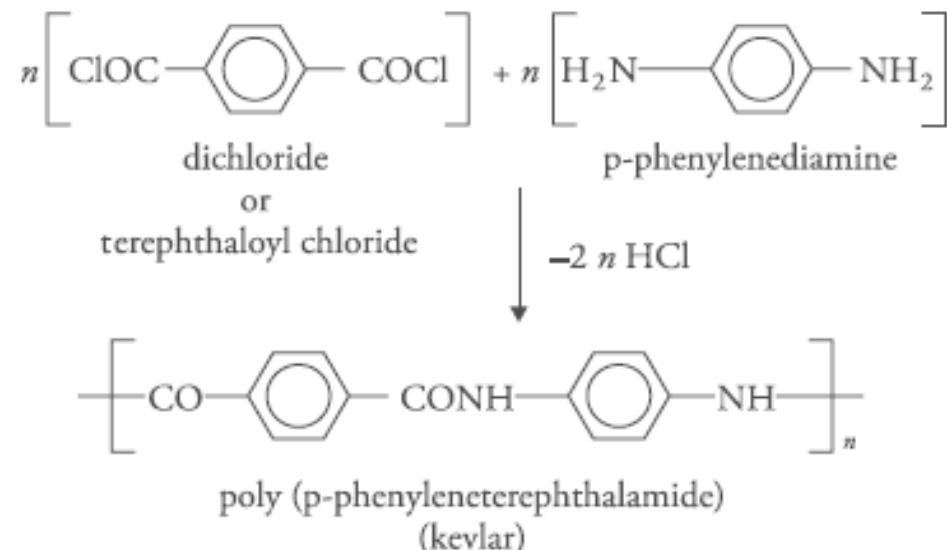


## 4. Liquid crystalline polymers

- Polymers that are capable of forming regions of highly ordered structure while in liquid phase.
- LCPs are very useful polymers because they have high mechanical strength at high temperatures.
- Extreme chemical resistance, inherent flame retardancy and good weatherability and are exceptionally inert.

➤ **Kevlar:** A very commonly known liquid crystalline polymer.

→ **Preparation:** It is an aromatic polyamide. It is prepared by the polycondensation of aromatic dichloride and aromatic diamines.



- **Properties**

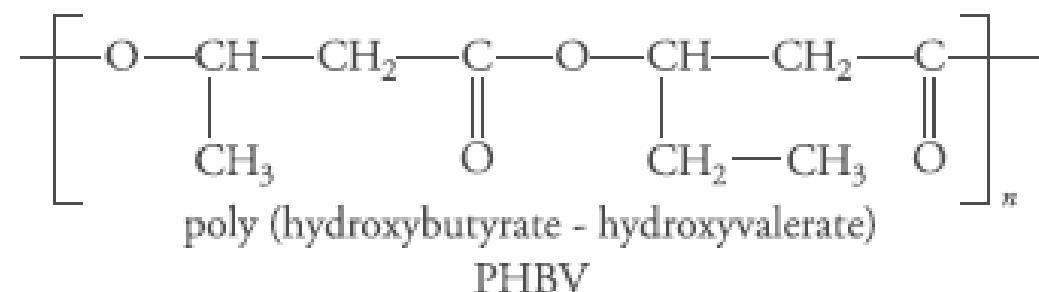
- Kevlar has **extraordinary mechanical properties**, high elastic modulus and high tensile strength.
- Kevlar is known for its ability to be spun into fibres that have five times the tensile strength of steel and 10 times that of Al on a weight to weight basis. The high tensile strength is due to extensive hydrogen bonding between the adjacent polymeric chains.
- It has **extreme chemical inertness, high heat stability and flexibility**. It is also extremely resistant to fire.

- **Applications**

- It is used in **the fabrication of protective wear including bullet-proof vests**.
- It is extensively **used in aerospace and aircraft industries, boat hulls, drum heads, sports equipments, car parts** (such as tyres, brakes, clutch linings), helmets, brake pads, ropes, cables, etc.
- LCPs are generally **used as reinforced (composite) materials with carbon or glass fibres**.

## 5. Biodegradable polymers

- Biodegradation is the degradation of a material by environmental factors such as sunlight, temperature changes or by the action of microbes (bacteria, fungi, etc.)
- Natural biodegradable polymers → rubber and cellulose (degradation by bacterial action)
- Synthetic biodegradable polymers → polyvinyl alcohol, hydroxyethylcellulose polymer, poly(hydroxybutyrate hydroxyvalerate) (PHBV)



## • Applications

- Biodegradable polymers find extensive use in the medical field. They are used commercially in tissue engineering and drug delivery field of biomedicine.
- Use in orthopaedic fixation devices. Biodegradable polymers are used to join fractured bones. They provide the required strength to the bone and after the bone heals and can take the load, they harmlessly degrade over time.
- In controlled drug delivery, the polymer slowly degrades into smaller fragments releasing the drug gradually and in a controlled manner.
- It is used in dental devices, biodegradable vascular stents, biodegradable soft tissue anchors, etc.
- Biodegradable polymers are also being increasingly used in the manufacture of plastic bags, toys and other plastic products. These polymers gradually degrade in the environment (or in landfills) and leave the environment 'greener'.

# THANK YOU

