Unit 1: Atomic Structure, Chemical Bonding & Solutions

Engineering Chemistry — DI01000071

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Unit 1 — Overview

Syllabus Topics

1.1 Atomic Structure (Orbits, Orbitals, e^- Config.)
1.2 Chemical Bonding (Ionic, Covalent, Metallic...)
1.3 Types of Solids
1.4 Solutions & Concentration Units
1.5 pH & Buffer Solutions
1.6 Degree of Ionization

Weightage: $\approx 14\%$

Teaching Hrs: ≈ 7 hrs

Section 1.1
Atomic Structure

Orbits vs Orbitals · Shapes of Orbitals · Quantum Numbers
Electronic Configuration · Pauli's Principle
Hund's Rule · Aufbau Principle

Orbits vs Orbitals

Orbit

- Circular/elliptical path
- 2D concept (Bohr model)
- Denoted: $n = 1, 2, 3 \ldots$
- Max. $2n^2$ electrons
- Fixed, well-defined path

Orbital

- 3D probability region
- Quantum mechanical concept
- Denoted: s, p, d, f
- Max. 2 electrons per orbital
- No definite boundary

Key Point

Orbit = outdated fixed path (Bohr); Orbital = modern 3D probability cloud (quantum model)

Shapes of Orbitals

s-Orbital

Spherical

1 per subshell

Max. 2 e^-

p-Orbital

Dumbbell

3 per subshell

Max. 6 e^-

d-Orbital

Double dumbbell

5 per subshell

Max. 10 e^-

Subshell Capacity

Subshell	s	p	d	f
# Orbitals	1	3	5	7
Max e^-	2	6	10	14

Pauli's Exclusion Principle

Statement

"No two electrons in an atom can have the same set of all **four quantum numbers**."

Four Quantum Numbers

- n — Principal (shell: 1, 2, 3...)
- l — Azimuthal (subshell: 0 to $n-1$)
- m_l — Magnetic (orientation: $-l$ to $+l$)
- m_s — Spin ($+\frac{1}{2}$ or $-\frac{1}{2}$)

Consequence

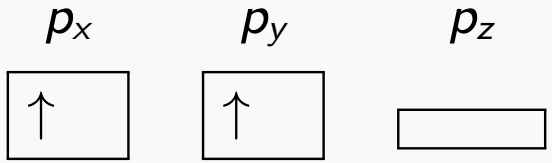
Two electrons in the same orbital must have **opposite spins** ($\uparrow\downarrow$) — max. **2 electrons per orbital**

Hund's Rule of Maximum Multiplicity

Statement

"Electrons occupy each orbital of a subshell *singly* before any pairing begins, with **parallel spins**."

Example: Carbon ($Z = 6$), config $2p^2$



Both electrons have **parallel spins** ($\uparrow\uparrow$) — NOT paired

Key Point

Half-filled (p^3, d^5) and fully-filled (p^6, d^{10}) subshells are **extra stable**

Aufbau Principle

Statement

"Electrons fill orbitals in order of **increasing energy**, governed by the $(n + l)$ rule."

Filling Order

$$1s \to 2s \to 2p \to 3s \to 3p \to 4s \to 3d \to 4p \to 5s \to 4d \to 5p \to 6s \to 4f \to 5d \ldots$$

$(n + l)$ Rule

- Orbital with **lower** $(n + l)$ fills first
- If $(n + l)$ equal, **lower** n fills first
- Ex: $4s$ $(n + l = 4)$ fills before $3d$ $(n + l = 5)$

Electronic Configuration: $Z = 1$ to 10

Z	Element	Configuration	Val. e^-
1	Hydrogen (H)	$1s^1$	1
2	Helium (He)	$1s^2$	2
3	Lithium (Li)	$[He]\,2s^1$	1
4	Beryllium (Be)	$[He]\,2s^2$	2
5	Boron (B)	$[He]\,2s^2\,2p^1$	3
6	Carbon (C)	$[He]\,2s^2\,2p^2$	4
7	Nitrogen (N)	$[He]\,2s^2\,2p^3$	5
8	Oxygen (O)	$[He]\,2s^2\,2p^4$	6
9	Fluorine (F)	$[He]\,2s^2\,2p^5$	7
10	Neon (Ne)	$[He]\,2s^2\,2p^6$	8

Note

He, Ne have **complete valence shells** — noble gas (inert) configuration

Electronic Configuration: $Z = 11$ to 20

Z	Element	Configuration	Val. e^-
11	Sodium (Na)	$[Ne]\,3s^1$	1
12	Magnesium (Mg)	$[Ne]\,3s^2$	2
13	Aluminium (Al)	$[Ne]\,3s^2\,3p^1$	3
14	Silicon (Si)	$[Ne]\,3s^2\,3p^2$	4
15	Phosphorus (P)	$[Ne]\,3s^2\,3p^3$	5
16	Sulphur (S)	$[Ne]\,3s^2\,3p^4$	6
17	Chlorine (Cl)	$[Ne]\,3s^2\,3p^5$	7
18	Argon (Ar)	$[Ne]\,3s^2\,3p^6$	8
19	Potassium (K)	$[Ar]\,4s^1$	1
20	Calcium (Ca)	$[Ar]\,4s^2$	2

Note

After Ar, $4s$ fills **before** $3d$ — Aufbau/$(n + l)$ rule

Electronic Configuration: $Z = 21$–30 (Transition Metals)

Z	Element	Configuration
21	Scandium (Sc)	$[Ar]\,3d^1\,4s^2$
22	Titanium (Ti)	$[Ar]\,3d^2\,4s^2$
23	Vanadium (V)	$[Ar]\,3d^3\,4s^2$
24	Chromium (Cr)	$[Ar]\,3d^{\mathbf{5}}\,4s^{\mathbf{1}}$ (exception)
25	Manganese (Mn)	$[Ar]\,3d^5\,4s^2$
26	Iron (Fe)	$[Ar]\,3d^6\,4s^2$
27	Cobalt (Co)	$[Ar]\,3d^7\,4s^2$
28	Nickel (Ni)	$[Ar]\,3d^8\,4s^2$
29	Copper (Cu)	$[Ar]\,3d^{\mathbf{10}}\,4s^{\mathbf{1}}$ (exception)
30	Zinc (Zn)	$[Ar]\,3d^{10}\,4s^2$

Cr & Cu Exceptions (PYQ – W'23)

Half-filled ($3d^5$) and fully-filled ($3d^{10}$) are **extra stable** — one e^- shifts from $4s \rightarrow 3d$

Section 1.2
Chemical Bonding

Octet Rule · Ionic · Covalent · Coordinate
Metallic · Hydrogen Bond · van der Waals

Octet Rule & Types of Chemical Bonds

Octet Rule

Atoms gain, lose, or share electrons to achieve **8 electrons** in the valence shell (noble gas configuration).

Bond Types

Bond	**Mechanism**	**Example**
Ionic	Electron transfer	NaCl, MgO
Covalent	Electron sharing	H_2, CH_4
Coordinate	One-sided e^- donation	NH_4^+, CO
Metallic	Electron sea model	Fe, Cu, Al
Hydrogen	Dipole–dipole (X-H$\cdots$Y)	H_2O, HF, DNA
van der Waals	Induced dipole	Noble gases, CH_4

Ionic Bond

Definition

Formed by complete **transfer of electrons** from metal to non-metal. Resulting oppositely charged ions attract electrostatically.

Example: NaCl (PYQ – Su'23)

$$\text{Na}\ (2,8,\mathbf{1}) \xrightarrow{-e^-} \text{Na}^+\ (2,8)$$

$$\text{Cl}\ (2,8,\mathbf{7}) \xrightarrow{+e^-} \text{Cl}^-\ (2,8,8)$$

$$\Rightarrow \text{Na}^+\text{Cl}^- \text{ — ionic lattice}$$

Properties

- High m.p. & b.p. (strong electrostatic forces)
- Conducts electricity in molten/dissolved state
- Soluble in polar solvents (water); brittle solid

Covalent Bond

Definition

Formed by **mutual sharing of electron pairs** between two non-metal atoms. Each atom contributes electrons.

Types

- **Single**: H–H (1 shared pair)
- **Double**: O=O (2 shared pairs)
- **Triple**: N≡N (3 shared pairs)

Properties

- Low m.p. & b.p.
- Poor conductors
- Non-polar solvent solubility
- Directional bond

PYQ (W'24)

Draw Lewis structure of ethene (C_2H_4); explain σ and π bonds.

Coordinate / Dative Bond

Definition

A covalent bond in which **both electrons are donated by one atom** (donor) to another (acceptor). Shown by arrow: donor $\rightarrow$ acceptor.

NH_4^+ Formation

NH_3 lone pair $\rightarrow H^+$

$\Rightarrow NH_4^+$ (ammonium ion)

All 4 N–H bonds identical

H_3O^+ Formation

H_2O lone pair $\rightarrow H^+$

$\Rightarrow H_3O^+$ (hydronium)

Key in acid-base chemistry

Key Distinction

Coordinate bond = special case of covalent bond; once formed, it is **indistinguishable** from ordinary covalent bond

Metallic Bond

Electron Sea Model

Metal atoms release valence electrons $\rightarrow$ form a **"sea" of delocalized electrons** surrounding a lattice of positive metal ions (kernels).

Properties Explained

Property	Reason
High conductivity	Free electrons move under electric field
Thermal conductivity	Free electrons transfer kinetic energy
Malleability/ductility	Layers slide; bond non-directional
Metallic lustre	Free electrons absorb & re-emit light
High tensile strength	Strong electrostatic attraction of ions to e^- sea

Hydrogen Bond

Definition

Electrostatic attraction between a **hydrogen atom bonded to a highly electronegative atom** (F, O, N) and a lone pair of another electronegative atom. Shown as X–H$\cdots$Y.

Types

Intermolecular:
H_2O, HF, NH_3

Intramolecular:
Salicylaldehyde, o-nitrophenol

Significance

- High b.p. of H_2O (100°C)
- DNA double helix
- Protein folding
- Ice less dense than water

van der Waals Forces

Overview

Weak intermolecular forces arising from **temporary or permanent dipoles**. Weakest of all intermolecular forces.

Three Types

Type	Interaction	Example
London / Dispersion	Instantaneous induced dipole–dipole	Noble gases, CH_4, I_2
Dipole–Dipole	Permanent dipole	HCl, SO_2
Dipole–Induced	Permanent + induced dipole	HCl–Ar mixture

Key Point

Strength order: London $<$ Dipole-Dipole $<$ H-bond $<$ Ionic/Covalent

Bond Comparison (PYQ – W'23, Su'24)

Bond	Mechanism	Strength	Example
Ionic	e^- transfer	Very strong	NaCl
Covalent	Shared pair	Strong	H_2, CH_4
Coordinate	One-sided donation	Strong	NH_4^+, BF_3
Metallic	e^- sea	Strong	Fe, Cu
Hydrogen	Dipole attraction	Moderate	H_2O, HF
van der Waals	Induced dipole	Weak	Noble gases

Exam Tip

A 7-mark question may ask to **compare any 3 bond types** with definition, formation, and properties. Prepare a table answer.

Section 1.3
Types of Solids

Ionic · Covalent / Network · Metallic · Molecular

Properties · Crystal Structures · Engineering Applications

Four Types of Solids

Type	Particles	Bond	Example
Ionic	Cations + anions	Ionic	NaCl, CaF_2
Covalent	Atoms (network)	Covalent	Diamond, SiO_2
Metallic	Metal ions + e^- sea	Metallic	Fe, Cu, Al
Molecular	Molecules	van der Waals, H-bond	Ice, CO_2, I_2

Highest m.p.: Covalent (diamond, 3550 °C)

Lowest m.p.: Molecular (CO_2 sublimes at −78 °C)

Crystal Structures: FCC, BCC, HCP

FCC

Face-Centred Cubic
APF: 74%
CN: 12
Ex: Cu, Al, Ni

BCC

Body-Centred Cubic
APF: 68%
CN: 8
Ex: Fe(α), Cr, W

HCP

Hexagonal Close-Packed
APF: 74%
CN: 12
Ex: Mg, Ti, Zn

APF = Atomic Packing Factor

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}}{\text{Total volume of unit cell}}$$

Simple cubic: 52%

Section 1.4
Solutions & Concentration Units

Molarity · Normality · Molality · Mole Fraction
% by Mass · % by Volume · pH & pOH

Solution Terminology

Term	Meaning
Solute	Substance dissolved (smaller amount)
Solvent	Dissolving medium (larger amount)
Solution	Homogeneous mixture of solute + solvent
Concentration	Amount of solute per unit volume/mass of solution
Dilute solution	Small amount of solute relative to solvent
Concentrated solution	Large amount of solute relative to solvent
Saturated	No more solute can dissolve at given temp.
Unsaturated	Can dissolve more solute
Supersaturated	More dissolved than saturation (unstable)

Molarity (M)

Definition & Formula

Molarity = no. of moles of solute per litre of solution

$$M = \frac{\text{moles of solute}}{\text{volume of solution (L)}} = \frac{w \times 1000}{M_w \times V_{\text{mL}}}$$

Solved Example (PYQ – Su'23)

Find molarity of 4 g NaOH in 500 mL solution.

$M_w(\text{NaOH}) = 40\,\text{g/mol}$

$$M = \frac{4 \times 1000}{40 \times 500} = \mathbf{0.2\,M}$$

Normality (N)

Definition & Formula

Normality = no. of gram equivalents of solute per litre of solution

$$N = \frac{\text{gram equivalents}}{\text{volume (L)}} = \frac{w \times 1000}{E_w \times V_{\text{mL}}}; \quad E_w = \frac{M_w}{n}$$

n-factor (equivalence factor)

Acid/Base	Compound	n-factor
Acid	HCl	1
Acid	H_2SO_4	2
Base	NaOH	1
Base	$Ca(OH)_2$	2

$$N = M \times n$$

Molality & Mole Fraction

Molality (m)

Moles of solute per **kg of solvent** (temperature-independent)

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{w \times 1000}{M_w \times W_s}$$

Mole Fraction (χ)

Ratio of moles of one component to total moles of all components

$$\chi_A = \frac{n_A}{n_A + n_B}; \quad \chi_B = \frac{n_B}{n_A + n_B}; \quad \chi_A + \chi_B = 1$$

Key

Molality & mole fraction are **independent of temperature**; molarity changes with temp.

Percentage Concentration Units

Unit	Formula	Abbr.
% by mass (w/w)	$\frac{w_{\text{solute}}}{w_{\text{soln}}} \times 100$	%(w/w)
% by volume (v/v)	$\frac{V_{\text{solute}}}{V_{\text{soln}}} \times 100$	%(v/v)
% by mass-volume (w/v)	$\frac{w_{\text{solute}}(\text{g})}{V_{\text{soln}}(\text{mL})} \times 100$	%(w/v)

Example

10 g NaCl dissolved in 90 g water:

$$\%(w/w) = \frac{10}{10+90} \times 100 = \mathbf{10\%}$$

pH and pOH

Definitions

$$\text{pH} = -\log[\text{H}^+] \qquad \text{pOH} = -\log[\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14 \quad (\text{at } 25^\circ\text{C})$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

pH Scale

Acidic (pH < 7)	**Neutral** (pH $= 7$)	**Basic** (pH > 7)
HCl, H_2SO_4	Pure water	NaOH, NH_3

Solved (PYQ – W'24)

$[\text{H}^+] = 0.001\,\text{M}$: $\text{pH} = -\log(10^{-3}) = \mathbf{3}$ (acidic)

pH Calculations — Strong Acids

Strong Acids (fully ionized)

$HA \rightarrow H^+ + A^-$ (100% ionization)

$[H^+] = C \times n$ (n = basicity)

Worked Examples

Solution	$[H^+]$	pH
0.1 M HCl	0.1 M	1.0
0.01 M HCl	0.01 M	2.0
0.1 M H_2SO_4	0.2 M	0.7
1 M NaOH ($\rightarrow$ pOH=0)	10^{-14} M	14.0

Rule

For diprotic acids (H_2SO_4, H_2CO_3): $[H^+] = 2C$ (if fully ionized)

Section 1.5
Degree of Ionization

Arrhenius Theory · Degree of Ionization

Factors Affecting Ionization · Ostwald's Dilution Law

Arrhenius Theory of Ionization

Theory (1887)

Acids, bases, and salts **dissociate into ions** when dissolved in water.

Acid

Produces $\mathbf{H^+}$ ions in water

$HCl \rightarrow H^+ + Cl^-$

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

Base

Produces $\mathbf{OH^-}$ ions in water

$NaOH \rightarrow Na^+ + OH^-$

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

Limitation

Valid only in **aqueous** solutions. Does not explain acidic/basic behaviour in non-aqueous solvents.

Degree of Ionization (α)

Definition & Formula

Fraction of dissolved electrolyte that ionizes

$$\alpha = \frac{\text{no. of moles ionized}}{\text{total moles dissolved}} \quad (0 \leq \alpha \leq 1)$$

Strong Electrolytes

$\alpha \approx 1$ (100%)

HCl, H_2SO_4,
NaOH, NaCl

Weak Electrolytes

$\alpha \ll 1$ ($< 5\%$)

CH_3COOH,
NH_4OH, HCN

PYQ (Su'24)

Define degree of ionization. State 4 factors affecting it.

Factors Affecting Degree of Ionization

Factor	Effect
Nature of solute	Strong electrolytes ionize $>$ weak electrolytes
Nature of solvent	Polar solvents (water) increase ionization
Concentration	α increases on dilution
Temperature	Higher temp $\Rightarrow$ higher α
Common ion effect	Adding common ion $\Rightarrow$ suppresses ionization
Dielectric constant	Higher ε of solvent $\Rightarrow$ higher α

Ostwald's Dilution Law

$$K_a = \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2 \text{ (when } \alpha \ll 1) \Rightarrow \alpha = \sqrt{K_a/C}$$

Section 1.6
Buffer Solutions

Definition · Types · Buffer Action
Henderson-Hasselbalch Equation · Applications

Buffer Solutions

Definition (PYQ – W'25, Su'25)

A solution that **resists change in pH** upon addition of small amounts of acid or base (or on dilution).

Acidic Buffer

pH < 7

Weak acid + its salt

$CH_3COOH + CH_3COONa$

pH ≈ 4.74

Basic Buffer

pH > 7

Weak base + its salt

$NH_4OH + NH_4Cl$

pH ≈ 9.25

Buffer Action & Henderson-Hasselbalch Equation

Mechanism (CH_3COOH/CH_3COONa)

On adding acid (H^+):

$CH_3COO^- + H^+ \rightarrow CH_3COOH$ (H^+ consumed)

On adding base (OH^-):

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Henderson-Hasselbalch Equation

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Applications of Buffer Solutions

Field	Buffer	pH
Blood (biological)	H_2CO_3/HCO_3^-	7.35–7.45
Pharmaceutical/drug	Various	Product-specific
Food preservation	Citric acid/citrate	3–5
Electroplating baths	Acetate/borate buffers	4–9
Analytical chemistry	Standard buffers	4.0, 7.0, 9.2

Blood Buffer (PYQ – W'25)

Blood pH must stay 7.35–7.45. Below 7.35 = **acidosis**; above 7.45 = **alkalosis** — both life-threatening.

Numericals: Molarity & Normality (PYQ – Su'25)

Problem 1

Find molarity of 9.8 g H_2SO_4 in 500 mL solution.

$M_w(H_2SO_4) = 98$, $M = \dfrac{9.8 \times 1000}{98 \times 500} = \mathbf{0.2\,M}$

Problem 2

Find normality of 4.9 g H_2SO_4 in 250 mL solution.

$E_w = 98/2 = 49$; $N = \dfrac{4.9 \times 1000}{49 \times 250} = \mathbf{0.4\,N}$

Relation

$N = M \times n\text{-factor} \quad \Rightarrow 0.4 = 0.2 \times 2$ ✓

Numerical: Buffer pH (PYQ – W'24)

Problem

Calculate pH of acetate buffer: $[CH_3COOH] = 0.1\,M$, $[CH_3COONa] = 0.1\,M$. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$

Solution

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$pH = 4.74 + \log\frac{0.1}{0.1} = 4.74 + 0 = \mathbf{4.74}$$

(Buffer with equal acid & salt concentration $\Rightarrow$ pH = pK_a)

All Concentration Units — Quick Reference

Unit	Formula	Note
Molarity (M)	$\frac{n_{\text{solute}}}{V_{\text{soln}}(\text{L})}$	Temp-dependent
Normality (N)	$\frac{\text{Gram equiv.}}{V(\text{L})}$	$N = M \times n$
Molality (m)	$\frac{n_{\text{solute}}}{m_{\text{solvent}}(\text{kg})}$	Temp-independent
Mole fraction	$\frac{n_A}{n_A + n_B}$	Dimensionless
%(w/w)	$\frac{w_s}{w_{\text{soln}}} \times 100$	Most common

Exam Strategy

Identify quantity asked $\rightarrow$ select formula $\rightarrow$ check units (g/mol, mL/L) before substituting.

Ostwald's Dilution Law

Statement

For a weak electrolyte $HA \rightleftharpoons H^+ + A^-$ at concentration C (mol/L):

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

For weak electrolytes ($\alpha \ll 1$): $K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$

PYQ Numerical (Su'23)

α of CH_3COOH at 0.1 M, $K_a = 1.8 \times 10^{-5}$:

$\alpha = \sqrt{1.8 \times 10^{-5}/0.1} = \sqrt{1.8 \times 10^{-4}} = \mathbf{1.34 \times 10^{-2}}$ (1.34%)

PYQ Discussion: 7-Mark Questions on Unit 1

Frequently Asked (All Papers)

1. Define & explain **buffer solution** with mechanism and buffer equation. (W'25, Su'25)
2. Compare **ionic, covalent, metallic** bonds. (W'23, Su'24)
3. Write electronic configuration of **Cr and Cu**; explain exceptions. (W'23)
4. Explain **Hund's rule** with example; state Pauli's exclusion principle. (Su'24)
5. Define molarity, normality, molality with formulas and numericals. (Su'23, W'25)
6. Explain **degree of ionization**; state factors affecting it. (Su'24, W'24)

Tip

Always write **definition + formula + example + application** for 7-mark answers.

Unit 1 — Key Formulas & Definitions

Topic	Formula / Key Fact
Max e^- in shell	$2n^2$
Molarity	$M = \frac{w \times 1000}{M_w \times V_{mL}}$
Normality	$N = M \times n$-factor
pH	$pH = -\log[H^+]$; pH+pOH=14
H-H Equation	$pH = pK_a + \log \frac{[Salt]}{[Acid]}$
Ostwald's Law	$\alpha = \sqrt{K_a/C}$ (dilute)
APF (FCC/HCP)	74%; BCC: 68%; SC: 52%

Next: Frames 46–60

Advanced topics: Lewis structures, colligative properties, PYQ pattern analysis, Unit 1 mind map

Lewis (Electron Dot) Structures

What is a Lewis Structure?

Representation of molecules/ions showing **all valence electrons** as dots and shared pairs as lines (bonds).

Steps to Draw

1. Count total valence electrons
2. Place least electronegative atom at centre
3. Form single bonds between all atoms
4. Complete octets of outer atoms using remaining e^-
5. If central atom lacks octet, form multiple bonds

PYQ (W'24)

Draw Lewis structures of: H_2O (2 lone pairs on O), NH_3 (1 lone pair on N), CO_2 (double bonds, linear).

Ethene (C_2H_4) – σ and π Bonds (PYQ – W'24)

Structure

$H_2C{=}CH_2$: each C is sp^2 hybridized

Double bond $= 1\sigma + 1\pi$

σ Bond

Head-on overlap

Stronger, shorter

Free rotation

π Bond

Lateral/side overlap

Weaker, longer

No free rotation

Bond Count Rule

Single bond $= 1\sigma$; Double bond $= 1\sigma{+}1\pi$; Triple bond $= 1\sigma{+}2\pi$

NaCl Crystal Structure (Ionic Solid)

Face-Centred Cubic Lattice

- Na^+ and Cl^- alternating in 3D FCC lattice
- Each ion surrounded by **6 oppositely-charged** ions (CN = 6)
- Unit cell contains 4 NaCl formula units
- Held by strong **electrostatic** (ionic) forces

Ionic Solid Properties

High m.p./b.p. · Hard but brittle · Non-conductor (solid)
Conducts in molten/dissolved state · Soluble in polar solvents

Diamond vs Graphite — Network (Covalent) Solids

Diamond

sp^3 hybridized C

3D network, tetrahedral

Hardest natural substance

Non-conductor

m.p. 3550 °C

Use: cutting tools, gems

Graphite

sp^2 hybridized C

Layered hexagonal sheets

Soft, lubricant

Good conductor (delocalized π)

m.p. >3500 °C

Use: electrodes, pencils

Key (PYQ – Su'24)

Both are allotropes of carbon. Diamond = insulator; Graphite = conductor due to delocalized electrons.

Anomalous Properties of Water (H-Bond Effects)

Why Water is Unusual

All anomalous properties of H_2O are due to **extensive H-bonding** between molecules.

Property	Explanation
High b.p. (100 °C)	H-bonds require extra energy to break
Ice less dense than water	Hexagonal open lattice in ice $\Rightarrow$ lower density
High surface tension	Strong intermolecular H-bonds
High specific heat capacity	Energy absorbed in breaking H-bonds
Universal solvent	Dipole nature dissolves polar/ionic substances

Quantum Numbers — Summary Table

QN	Symbol	Values	Determines
Principal	n	1, 2, 3, ...	Shell, energy, size
Azimuthal	l	0 to $n-1$	Shape of orbital
Magnetic	m_l	$-l$ to $+l$	Orientation in space
Spin	m_s	$+\frac{1}{2}, -\frac{1}{2}$	Electron spin

Example: 2p electron

$n = 2,\ l = 1,\ m_l \in \{-1, 0, +1\},\ m_s = \pm\frac{1}{2}$

Three $2p$ orbitals: $2p_x$, $2p_y$, $2p_z$ — each holds 2 e^-

Colligative Properties of Solutions

Definition

Properties that depend only on the **number of solute particles**, not their nature.

Four Colligative Properties

Property	Formula / Effect
Vapour pressure lowering	$\Delta P = \chi_{\text{solute}} \cdot P^{\circ}$
Boiling point elevation	$\Delta T_b = K_b \cdot m$
Freezing point depression	$\Delta T_f = K_f \cdot m$
Osmotic pressure	$\pi = MRT$

Application

Anti-freeze (ethylene glycol in water): lowers freezing point by $\Delta T_f = K_f \cdot m$

Ionic vs Covalent vs Metallic — Property Comparison

Property	Ionic	Covalent	Metallic
M.p./B.p.	High	Low–High	High
Conductivity	Molten/soln.	Poor	Excellent
Solubility	Polar solvents	Non-polar solvents	Insoluble
Brittleness	Brittle	Varies	Ductile
Bonding	Electrostatic	Shared pairs	e^- sea
Example	NaCl	CH_4, Diamond	Fe, Cu

PYQ Practice: Short-Answer (2-Mark Questions)

Frequently Asked Definitions

Q1 Define molarity and give its SI unit.
Q2 State Hund's rule of maximum multiplicity.
Q3 What is a buffer solution? Give one example.
Q4 Define degree of ionization.
Q5 Write electronic configuration of Cr ($Z = 24$).
Q6 Distinguish between orbit and orbital.
Q7 State Aufbau principle.
Q8 What is coordinate bond? Give example.

Tip

2-mark answers: 2–3 lines max. Use **definition + example** format.

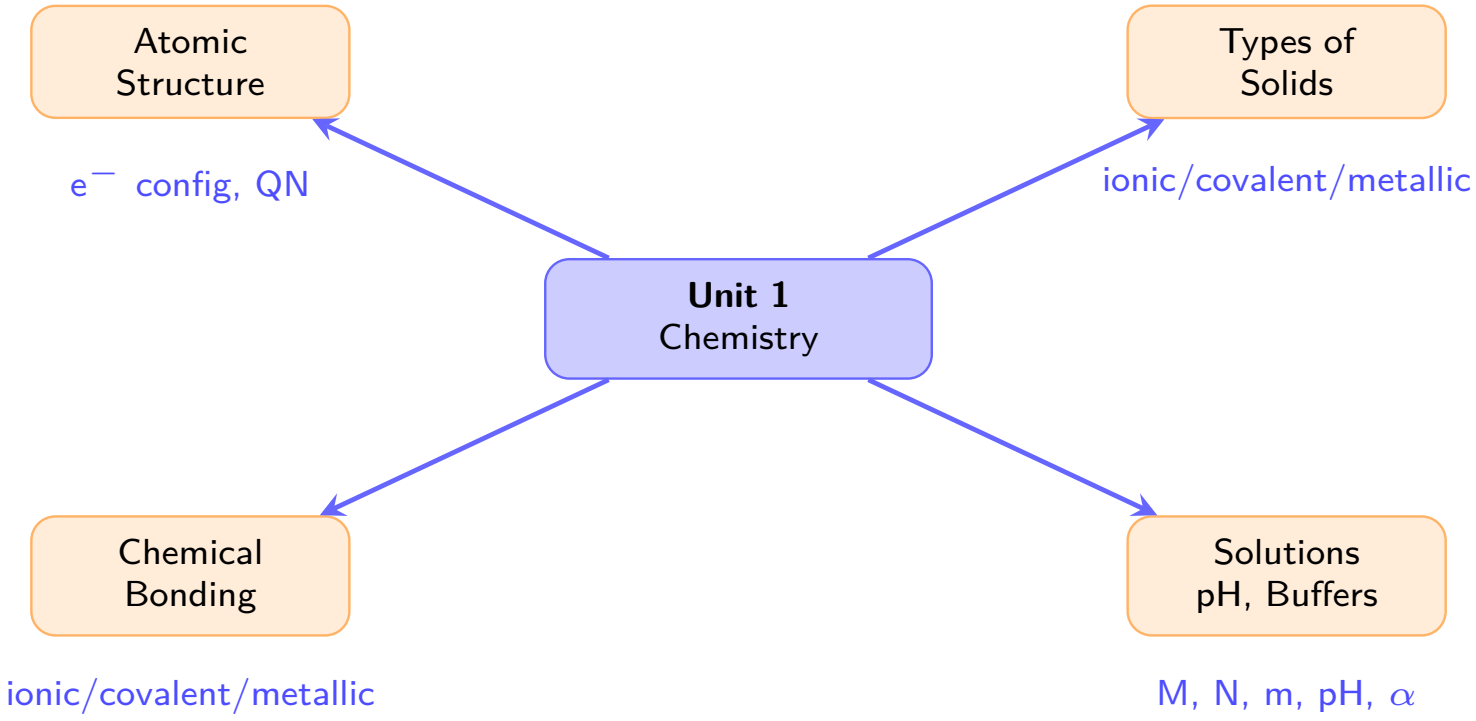
Unit 1 — PYQ Pattern Analysis

Topic	Su23	W23	Su24	W24	Su25	W25
Electronic config.	✓	✓	✓		✓	
Chemical bonding		✓	✓	✓		
Molarity/Normality	✓			✓	✓	
pH calculations		✓		✓		✓
Buffer solutions			✓			✓
Degree of ionization			✓			
Types of solids				✓	✓	

High Probability

Chemical bonding, molarity numericals, and buffer solutions appear in **almost every paper**.

Unit 1 — Mind Map



Unit 1 — Exam Tips

✓ Do's

- Write Cr/Cu config with reason
- Mention units in numericals
- Draw diagrams for bonds
- State all 3 quantum numbers in electronic config questions
- Use H-H equation for buffer pH

✗ Don'ts

- Don't confuse orbit vs orbital
- Don't swap molarity and molality
- Don't forget n-factor in normality
- Don't leave numericals without final box
- Don't mix acidic/basic buffer compositions

Time Allocation

7-mark: $\sim$8 min · 4-mark: $\sim$4 min · 2-mark: $\sim$2 min

Normality Numericals Practice (PYQ – W'25)

Problem 1

Find normality of 6.3 g HNO_3 in 200 mL solution.

$M_w = 63,\ n = 1,\ E_w = 63$

$$N = \frac{6.3 \times 1000}{63 \times 200} = \mathbf{0.5\ N}$$

Problem 2

Find normality of 4 g NaOH in 500 mL.

$M_w = 40,\ n = 1,\ E_w = 40$

$$N = \frac{4 \times 1000}{40 \times 500} = \mathbf{0.2\ N}$$

pH of Weak Acid — Numerical (PYQ – Su'25)

Problem

Find pH of 0.1 M CH_3COOH solution.
$K_a = 1.8 \times 10^{-5}$

Solution (step-by-step)

Step 1: $\alpha = \sqrt{K_a/C} = \sqrt{1.8 \times 10^{-5}/0.1} = 1.34 \times 10^{-2}$

Step 2: $[H^+] = C\alpha = 0.1 \times 1.34 \times 10^{-2} = 1.34 \times 10^{-3}$ M

Step 3: $\text{pH} = -\log(1.34 \times 10^{-3}) = 3 - \log(1.34) = 3 - 0.127 = \mathbf{2.87}$

Unit 1 Complete — Preview of Unit 2

Unit 1 Covered

- ✓ Atomic structure, quantum numbers, electronic configuration
- ✓ Ionic, covalent, coordinate, metallic, H-bond, van der Waals
- ✓ Types of solids, crystal structures (FCC/BCC/HCP)
- ✓ Molarity, normality, molality, mole fraction, % concentration
- ✓ pH, pOH, buffer solutions, degree of ionization

Unit 2: Electrochemistry (Coming Next)

Oxidation & Reduction · Electrochemical Cells

Electrode Potential · Nernst Equation

Conductance · Faraday's Laws · Electrolysis Applications

Unit 2: Electrochemistry

Engineering Chemistry — DI01000071

Milav Dabgar

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April 2, 2026

Unit 2 — Overview

Syllabus Topics

2.1 Oxidation & Reduction (Redox)
2.2 Electrochemical Cells
2.3 Standard Electrode Potential & EMF
2.4 Nernst Equation
2.5 Conductance & Kohlrausch's Law
2.6 Faraday's Laws of Electrolysis
2.7 Applications of Electrolysis

Weightage: $\approx 14\%$

Teaching Hrs: ≈ 7 hrs

Section 2.1
Oxidation & Reduction

Oxidation · Reduction · Redox Reactions · Oxidation Numbers

OIL RIG: Oxidation Is Loss, Reduction Is Gain

Oxidation & Reduction — Electronic Concept

Oxidation

Loss of electrons

Increase in oxidation state

Example:
$Zn \rightarrow Zn^{2+} + 2e^{-}$

Oxidation = **O**-**I**-**L**

Reduction

Gain of electrons

Decrease in oxidation state

Example:
$Cu^{2+} + 2e^{-} \rightarrow Cu$

Reduction = **R**-**I**-**G**

OIL RIG Mnemonic

Oxidation **I**s **L**oss **R**eduction **I**s **G**ain — always occur simultaneously

Redox Reactions

Definition

Reactions involving **simultaneous oxidation and reduction**. The substance that loses electrons is the **reducing agent**; the substance that gains electrons is the **oxidizing agent**.

Example: $Zn + CuSO_4$ (PYQ – Su'23)

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

$Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation; Zn = reducing agent)

$Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction; Cu^{2+} = oxidizing agent)

Oxidation Numbers — Rules

Rules for Assigning Oxidation Number

R1	Free element: ON $= 0$ (e.g., Fe, O_2, Cl_2)
R2	Monoatomic ion: ON $=$ charge ($Na^+ = +1$, $Cl^- = -1$)
R3	Oxygen: ON $= -2$ (except peroxides: -1; OF_2: $+2$)
R4	Hydrogen: ON $= +1$ (except metal hydrides: -1)
R5	Sum of ON in compound $= 0$; in ion $=$ ion charge

Example: $K_2Cr_2O_7$

$$2(+1) + 2x + 7(-2) = 0 \Rightarrow x = +6$$

Cr has oxidation number **+6**

Section 2.2
Electrochemical Cells

Galvanic Cell (Daniel Cell) · Electrolytic Cell
Salt Bridge · Cell Notation · EMF

Galvanic Cell — Daniel Cell (PYQ – W'23, Su'24)

Construction

Anode (−): Zn rod in $ZnSO_4$ solution

Cathode (+): Cu rod in $CuSO_4$ solution

Connected by **salt bridge** and external wire

Reactions

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

Overall: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Cell notation: $Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$

EMF

$E_{cell} = E_{cathode} - E_{anode} = 0.34 - (-0.76) = \mathbf{1.10\,V}$

Salt Bridge — Functions & Composition

What is a Salt Bridge?

A U-shaped tube filled with concentrated **KCl or NH_4NO_3 in agar-agar** gel, connecting the two half-cells.

Functions

1. Completes the internal circuit by allowing ion flow
2. Maintains **electrical neutrality** in both half-cells
3. Prevents direct mixing of the two electrolyte solutions
4. Minimises liquid junction potential

Without Salt Bridge

Cell reaction stops quickly due to charge build-up; no sustained current flow.

Electrolytic Cell

Definition

A cell in which **electrical energy drives a non-spontaneous** chemical (redox) reaction. Requires external power supply.

Anode (+)

Connected to positive terminal of battery

Oxidation occurs

Anions discharge here

Cathode (−)

Connected to negative terminal of battery

Reduction occurs

Cations discharge here

Applications

Electroplating, electro-refining, electrometallurgy, electrolysis of water/NaCl

Galvanic vs Electrolytic Cell

Feature	Galvanic Cell	Electrolytic Cell
Energy conversion	Chemical $\rightarrow$ Electrical	Electrical $\rightarrow$ Chemical
Reaction	Spontaneous ($\Delta G < 0$)	Non-spontaneous ($\Delta G > 0$)
External supply	Not required	Required
Anode polarity	Negative ($-$)	Positive ($+$)
Cathode polarity	Positive ($+$)	Negative ($-$)
Example	Daniel cell, battery	Electroplating, electrolysis

Standard Electrode Potential & Electrochemical Series

Definition

Potential of a half-cell measured relative to **Standard Hydrogen Electrode (SHE)** at 298 K, 1 atm, 1 M concentration.

Selected Reduction Potentials (E°/V)

Half-reaction	E° (V)
$Li^+ + e^- \rightarrow Li$	-3.04
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$2H^+ + 2e^- \rightarrow H_2$	0.00 (SHE)
$Cu^{2+} + 2e^- \rightarrow Cu$	$+0.34$
$Ag^+ + e^- \rightarrow Ag$	$+0.80$

Standard Hydrogen Electrode (SHE)

Construction

- Platinum electrode coated with platinum black
- Immersed in 1 M HCl ($H^+ = 1\,M$)
- H_2 gas bubbled at 1 atm, 298 K
- Standard potential = **0.00 V** (reference)

Half-Cell Reaction

$$\text{Oxidation: } H_2 \rightarrow 2H^+ + 2e^- \quad (E^\circ = 0.00\,V)$$

$$\text{Reduction: } 2H^+ + 2e^- \rightarrow H_2 \quad (E^\circ = 0.00\,V)$$

Nernst Equation (PYQ – W'24, Su'25)

Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q \quad \text{(at 298K)}$$

Terms

E°_{cell}	Standard EMF (V)
R	Gas constant (8.314 J/mol K)
T	Temperature (K)
n	No. of electrons transferred
F	Faraday's constant (96485 C/mol)
Q	Reaction quotient

Nernst Equation — Solved Example (PYQ – W'24)

Problem

Calculate E_{cell} for Daniel cell at 298 K when $[Zn^{2+}] = 0.1\,\text{M}$ and $[Cu^{2+}] = 0.01\,\text{M}$.
$E^\circ(Zn^{2+}/Zn) = -0.76\,\text{V}; \quad E^\circ(Cu^{2+}/Cu) = +0.34\,\text{V}$

Solution

$E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10\,\text{V}; \quad n = 2$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.1}{0.01} = 10$$

$$E = 1.10 - \frac{0.0592}{2}\log 10 = 1.10 - 0.0296 = \mathbf{1.07\,V}$$

Section 2.5
Conductance of Electrolytic Solutions

Resistance · Conductance · Conductivity

Molar Conductance · Kohlrausch's Law

Resistance, Conductance & Conductivity

Quantity	Definition	Formula	Unit
Resistance (R)	Opposition to current flow	$R = \rho\, l/A$	Ω
Conductance (G)	Reciprocal of resistance	$G = 1/R$	S (siemen)
Resistivity (ρ)	Resistance per unit cross-section	$\rho = R\,A/l$	Ω·cm
Conductivity (κ)	Conductance per unit length	$\kappa = 1/\rho$	S/cm

Key

κ increases with concentration (more ions). But molar conductance *decreases* with concentration due to interionic attraction.

Molar Conductance (Λ_m)

Definition & Formula

Conductance of a solution containing **1 mole of electrolyte** placed between electrodes 1 cm apart

$$\Lambda_m = \frac{\kappa \times 1000}{C} \quad (\mathrm{S\,cm^2/mol})$$

where C is concentration in mol/L

Strong Electrolyte

Λ_m increases slowly
on dilution (Kohlrausch)

Weak Electrolyte

Λ_m rises sharply
at high dilution (ionization)

Kohlrausch's Law of Independent Migration

Statement (PYQ – W'25)

"At infinite dilution, each ion migrates **independently** and contributes a definite amount to the molar conductance."

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

Application: CH_3COOH (PYQ – Su'24)

$\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(HCl) + \Lambda_m^\circ(CH_3COONa) - \Lambda_m^\circ(NaCl)$

Used to find Λ_m° of **weak electrolytes** (cannot be measured directly)

Applications of Conductance Measurements

Application	Principle
Degree of ionization	$\alpha = \Lambda_m / \Lambda_m^\circ$
Ionization constant (K_a)	$K_a = C\alpha^2/(1-\alpha)$
Solubility of sparingly sol. salt	From conductivity of saturated soln.
Conductometric titration	Endpoint = minimum conductance
Water purity testing	Pure water: very low conductivity

Conductometric Titration

Strong acid + strong base: conductance drops to minimum at equivalence point, then rises with excess base.

Section 2.6
Faraday's Laws of Electrolysis

First Law ($m \propto Q$) · Second Law ($m \propto E_w$)

Faraday's Constant $F = 96485\,\mathrm{C/mol} \approx 96500\,\mathrm{C/mol}$

Faraday's First Law of Electrolysis

Statement

"The mass of substance deposited/liberated at an electrode is **directly proportional to the quantity of charge** passed."

$$m = Z \cdot Q = Z \cdot I \cdot t$$

Terms

m	Mass deposited (g)
Z	Electrochemical equivalent (g/C)
Q	Charge $= I \times t$ (coulombs)
I	Current (A); $t =$ time (s)
Z	$= E_w/F = M_w/(n \cdot F)$

Faraday's Second Law of Electrolysis

Statement

"When the same quantity of charge is passed through different electrolytic solutions, the masses deposited are **proportional to their equivalent weights**."

$$\frac{m_1}{m_2} = \frac{E_{w1}}{E_{w2}}$$

Example (PYQ – Su'23)

Same charge through $CuSO_4$ & $AgNO_3$ in series:

$$\frac{m_{Cu}}{m_{Ag}} = \frac{E_w(Cu)}{E_w(Ag)} = \frac{31.75}{108} = 0.294$$

If 1.08 g Ag deposited $\Rightarrow$ 0.318 g Cu deposited

Faraday's Law Numericals (PYQ – W'25, Su'25)

Problem 1

Find mass of Cu deposited by 2 A for 1 hr from $CuSO_4$.

$Q = 2 \times 3600 = 7200\,\text{C}; \quad E_w(\text{Cu}) = 31.75$

$$m = \frac{E_w \times Q}{96500} = \frac{31.75 \times 7200}{96500} = \mathbf{2.37\,g}$$

Problem 2

Find time to deposit 1 g Ag by 0.5 A from $AgNO_3$.

$$m = ZQ \Rightarrow t = \frac{m \times 96500}{E_w \times I} = \frac{1 \times 96500}{108 \times 0.5} = \mathbf{1787\,s}$$

Electrolysis of Water

Setup

Dilute H_2SO_4 or NaOH used to increase conductivity. Pt electrodes.

Reactions

Cathode (−): $4H^+ + 4e^- \rightarrow 2H_2 \uparrow$ (reduction)

Anode (+): $2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^-$ (oxidation)

Overall: $2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2$

Volume Ratio

$H_2 : O_2 = \mathbf{2 : 1}$ (by volume). H_2 collected at cathode; O_2 at anode.

Electro-Refining (PYQ – W'23, Su'24)

Principle

Purification of metals using electrolysis. **Impure metal = anode**; **pure metal = cathode**; electrolyte = salt of same metal.

Copper Refining

Anode: Impure Cu $\rightarrow Cu^{2+} + 2e^-$ (dissolves)

Cathode: $Cu^{2+} + 2e^- \rightarrow$ Cu (pure, deposits)

Anode mud: Ag, Au, Pt settle below anode (valuable by-product)

Electrolyte: $CuSO_4 + H_2SO_4$

Other Metals

Ag, Au, Ni, Pb, Zn are also refined by same principle.

Electroplating (PYQ – Su'23, W'24)

Principle

Depositing a thin layer of metal on another object to improve **appearance, corrosion resistance, or surface hardness**. Object to be plated = **cathode**; plating metal = **anode**.

Silver Plating Example

Component	Detail
Cathode	Object to be plated (e.g., Cu spoon)
Anode	Pure silver rod
Electrolyte	AgCN in KCN solution
Reaction (cathode)	$Ag^+ + e^- \rightarrow Ag$
Reaction (anode)	$Ag \rightarrow Ag^+ + e^-$

Electrometallurgy

Definition

Extraction of metals from their ores using electrolysis. Used for highly electropositive metals (cannot be reduced by carbon/H_2).

Important Examples

Metal	Ore/Source	Process
Al	Alumina (Al_2O_3)	Hall-Héroult (molten cryolite)
Na	NaCl (molten)	Down's cell
Mg	$MgCl_2$ (molten)	Electrolysis of molten salt
Cu	$CuSO_4$ (aq.)	Electrolytic deposition

Electrolysis of Aqueous NaCl (Brine)

Reactions (PYQ – Su'24)

Cathode: $2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-$

Anode: $2Cl^- \rightarrow Cl_2 \uparrow + 2e^-$

Overall (Chlor-alkali process):
$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$

Products & Uses

Cl_2: PVC, bleaching powder, disinfectants

H_2: Fuel, NH_3 synthesis, hydrogenation

NaOH: Soap, paper, textiles, alumina processing

Unit 2 — Mid-Point Summary (Frames 1–30)

Topic	Key Point
Oxidation/Reduction	OIL RIG; simultaneous
Daniel cell	$E = 1.10\,\text{V}$; Zn anode, Cu cathode
Salt bridge	Maintains neutrality
SHE	Reference; $E^\circ = 0.00\,\text{V}$
Nernst equation	$E = E^\circ - (0.0592/n)\log Q$
Conductance	$G = 1/R$; $\kappa = 1/\rho$
Kohlrausch's law	$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$
Faraday's 1st law	$m = ZIt$
Faraday's 2nd law	$m_1/m_2 = E_{w1}/E_{w2}$
Electro-refining	Impure anode $\rightarrow$ pure cathode

EMF & Gibbs Free Energy

Relationship

$\Delta G = -nFE_{\text{cell}}$ (at standard conditions: $\Delta G^\circ = -nFE^\circ_{\text{cell}}$)

Symbol	Meaning
n	number of electrons transferred
F	Faraday constant $= 96500\,\text{C mol}^{-1}$
E_{cell}	cell EMF (V)
ΔG	Gibbs free energy (J)

Spontaneity

$E > 0$	$\Delta G < 0$ (spontaneous)
$E = 0$	$\Delta G = 0$ (equilibrium)
$E < 0$	$\Delta G > 0$ (non-spont.)

Equilibrium Link

$$\Delta G^\circ = -RT \ln K$$

$$\Rightarrow E^\circ = \frac{RT}{nF} \ln K$$

At 298 K: $E^\circ = \dfrac{0.0592}{n} \log K$

Electrochemical Series — Applications

Standard Reduction Potential Order

$Li^+ < K^+ < Na^+ < Mg^{2+} < Al^{3+} < Zn^{2+} < Fe^{2+} < Ni^{2+} < H^+ < Cu^{2+} < Ag^+ < Au^{3+}$

Application	Rule
Displacement reactions	Higher activity metal displaces lower (Zn displaces Cu from $CuSO_4$)
Predicting cell reaction	More –ve E° = anode; more +ve = cathode
Electroplating order	Use cathode as base metal, anode as coating metal
Corrosion tendency	Metals above H in series dissolve more readily

Example: Can Zn displace Cu?

$E^\circ(Zn^{2+}/Zn) = -0.76\,V$, $E^\circ(Cu^{2+}/Cu) = +0.34\,V$

$E^\circ_{cell} = 0.34 - (-0.76) = +1.10\,V > 0$ **Yes, spontaneous.**

Concentration Cells

Definition

A cell in which **both electrodes are identical** but immersed in solutions of **different concentrations**. EMF arises due to concentration difference (not chemical difference).

Cell Notation

$\mathrm{Cu}|c_1||\mathrm{Cu}^{2+}|c_2|\mathrm{Cu}$

Anode: lower conc. (c_1)

Cathode: higher conc. (c_2)

Nernst for Conc. Cell

$$E = \frac{0.0592}{n} \log \frac{c_2}{c_1}$$

$E^\circ = 0$ (same electrodes)

Example: Cu–Cu cell, $c_1 = 0.01\,\mathrm{M}$, $c_2 = 0.1\,\mathrm{M}$

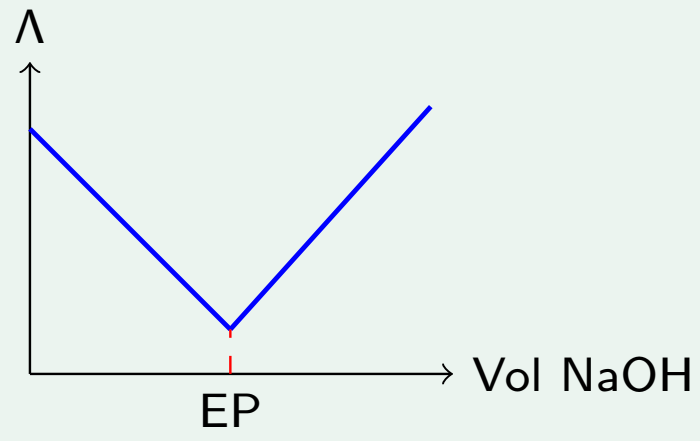
$$E = \frac{0.0592}{2} \log \frac{0.1}{0.01} = 0.0296 \times 1 = \mathbf{0.0296}\,\mathrm{V}$$

Conductometric Titration

Principle

Conductance of a solution changes as titrant is added. End point determined from **change in slope** of conductance vs. volume graph — no indicator needed.

Strong Acid–Strong Base



Graph Shape

Titration	**Shape**
Strong acid–strong base	V-shaped
Weak acid–strong base	Falling, then rise
Salt soln–precipitation	V-shaped

Advantages: Suitable for coloured/turbid solutions; applicable to very dilute solutions; precise end point detection.

Chromium & Nickel Electroplating

Chromium Plating

Electrolyte	CrO_3 in H_2SO_4
Anode	Lead (Pb)
Cathode	Object to plate
Thickness	0.25 μm (decor)
	25 μm (hard chrome)

Uses: Auto parts, tools, shafts (hard/wear-resistant)

Nickel Plating

Electrolyte	$NiSO_4 + NiCl_2$ (Watts bat
Anode	Nickel metal
Cathode	Object to plate
pH	3.5–4.5

Uses: Base coat under chrome; sanitary fittings; corrosion protection

Key Reactions — Chromium

Cathode: $Cr_2O_7^{2-} + 14H^+ + 12e^- \rightarrow 2Cr + 7H_2O$

Zinc Electroplating & Galvanizing

Zinc Electroplating

Item	Material	Role
Electrolyte	$ZnSO_4$ solution	Zn^{2+} source
Anode	Zinc metal	Dissolves
Cathode	Iron/steel	Coated

Cathode rxn: $Zn^{2+} + 2e^- \rightarrow Zn$

Anode: $Zn - 2e^- \rightarrow Zn^{2+}$

Hot-Dip Galvanizing

Steel dipped in molten Zn (450 °C). Zinc–iron alloy layer forms. Better adhesion; thicker coat. **Used for**: roofing sheets, pipes, buckets, nails.

Why Zinc Protects

Zn is more active than Fe. Acts as **sacrificial anode** — even if coating is scratched, Zn corrodes preferentially, protecting Fe.

Anodizing of Aluminium

What is Anodizing?

An **electrochemical process** that thickens the natural Al_2O_3 oxide layer on aluminium surface. Unlike electroplating, the metal is the **anode**.

Process

Electrolyte	H_2SO_4 (15–20%)
Anode	Aluminium object
Cathode	Lead / Al
Reaction	$2Al + 3H_2O \rightarrow Al_2O_3 + 6H$

Advantages

- Hard, corrosion-resistant surface
- Porous $\rightarrow$ can be dyed (coloured finishes)
- Better paint adhesion
- Electrical insulation

Applications: Aircraft parts, window frames, cookware, consumer electronics (iPhone body)

Corrosion — Electrochemical Nature (Preview)

Definition

Corrosion is the **gradual deterioration** of metals by electrochemical reaction with environment (moisture, O_2, acids).

Rusting of Iron

Anode (Fe, oxidation):

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Cathode (O_2, reduction):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

$$\rightarrow Fe_2O_3 \cdot xH_2O \text{ (rust)}$$

Electrochemical Cell in Rust

Different regions of same metal act as micro-anode and micro-cathode due to:

- Stress differences
- Concentration differences
- Grain boundary effects

(Detail in Unit 3)

Electrochemical Equivalent Values

Electrochemical Equivalent $Z = M/(nF)$ (g C^{-1})

Element	M (g/mol)	n	Z $\times 10^{-4}$	Reaction
Silver (Ag)	107.87	1	11.18	$Ag^{+} + e^{-} \rightarrow Ag$
Copper (Cu)	63.55	2	3.29	$Cu^{2+} + 2e^{-} \rightarrow Cu$
Gold (Au)	197.0	3	6.81	$Au^{3+} + 3e^{-} \rightarrow Au$
Nickel (Ni)	58.69	2	3.04	$Ni^{2+} + 2e^{-} \rightarrow Ni$
Zinc (Zn)	65.38	2	3.39	$Zn^{2+} + 2e^{-} \rightarrow Zn$
Aluminium (Al)	26.98	3	0.93	$Al^{3+} + 3e^{-} \rightarrow Al$
Hydrogen (H)	1.008	1	0.104	$H^{+} + e^{-} \rightarrow \frac{1}{2}H_2$

Use in Faraday's First Law

$m = ZIt = Z \times Q$ where $Q = It$ (charge in coulombs)

Solved EMF & ΔG Numerical

Problem (PYQ W'24 type)

Calculate E°_{cell} and ΔG° for: $\text{Zn}\,|\,\text{Zn}^{2+}(1\text{M})\,||\,\text{Cu}^{2+}(1\text{M})\,|\,\text{Cu}$
Given: $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76\,\text{V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34\,\text{V}$

Solution

Step 1: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = +1.10\,\text{V}$

Step 2: $n = 2$, $F = 96500\,\text{C mol}^{-1}$

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.10$

$$\boxed{\Delta G^\circ = -212300\,\text{J mol}^{-1} = -212.3\,\text{kJ mol}^{-1}}$$

$\Delta G^\circ < 0$ confirms the reaction is **spontaneous**.

Conductance Numericals (PYQ)

Q1 (PYQ Su'24): Molar Conductance

Conductivity of 0.02 M KCl $= 2.768 \times 10^{-3}$ S cm^{-1}. Find Λ_m.

$$\Lambda_m = \frac{\kappa \times 1000}{C} = \frac{2.768 \times 10^{-3} \times 1000}{0.02}$$

$$\boxed{\Lambda_m = 138.4 \text{ S cm}^2\text{mol}^{-1}}$$

Q2 (PYQ W'25): Kohlrausch's Law

$$\Lambda_m^\infty(CH_3COOH) = \Lambda_{H^+}^\infty + \Lambda_{CH_3COO^-}^\infty$$
$$= 349.6 + 40.9 = 390.5 \text{ S cm}^2\text{mol}^{-1}$$

If Λ_m at 0.05 M $= 7.36$, degree of dissociation:

$$\alpha = \frac{7.36}{390.5} = \mathbf{0.0188} \ (1.88\%)$$

Applications of Electrolysis — Summary

Application	Electrolyte	Cathode	Anode
Electroplating (Cu)	$CuSO_4 + H_2SO_4$	Object (coated)	Pure Cu
Electro-refining	Crude metal salt	Pure metal	Crude metal
Electroplating (Ag)	$KAg(CN)_2$	Object	Pure Ag
Electroplating (Cr)	$CrO_3 + H_2SO_4$	Object	Pb (inert)
Anodizing (Al)	H_2SO_4	Pb/Al	Al object
Chlor-alkali	NaCl brine	Fe ($H_2\uparrow$)	C ($Cl_2\uparrow$)
Water splitting	Dil. H_2SO_4	Pt ($H_2\uparrow$)	Pt ($O_2\uparrow$)
Electroforming	Metal salt	Mandrel	Metal

Remember: Cathode = reduction = deposition; Anode = oxidation = dissolution (active) or gas evolution (inert)

PYQ 7-Mark Questions — Electrochemistry

Frequently Asked Long Questions

Question	Papers
Describe Daniel cell with reactions and cell notation	W'23, Su'24
Explain electroplating of copper with neat diagram	Su'23, W'24
State and explain Faraday's laws with numericals	W'25, Su'25
Explain electrolysis of NaCl brine (chlor-alkali)	Su'24, W'23
Explain electro-refining of copper; what is anode mud?	W'23, Su'24
Write Nernst equation; derive and solve numerical	W'24, Su'25
Explain Kohlrausch's law and its applications	W'25, Su'24

Strategy

7-mark answers need: Definition + Diagram + Reactions/Formula + Example/Numerical + Conclusion

Unit 2 PYQ Pattern Analysis

Topic	Su'23	W'23	Su'24	W'24	Su'25 / W'25
Daniel cell	2	7	7	2	2
Nernst equation	—	2	2	7	7
Faraday's laws	7	2	2	2	7
Electroplating	7	7	2	7	2
Electrolysis NaCl	2	7	7	2	2
Conductance	2	2	7	2	7
Kohlrausch's law	—	—	7	2	7
Oxidation no.	2	2	2	2	2
Electro-refining	2	7	7	2	2

Top 3 to master: Faraday's laws + Nernst + Electroplating — appear in every paper as 7-mark

Unit 2 — Key Formulas Summary

Formula	Variables
$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$	standard or actual EMF
$E = E^\circ - \dfrac{0.0592}{n} \log Q$	Nernst (298 K)
$\Delta G^\circ = -nFE^\circ$	n=electrons, F=96500
$m = ZIt = \dfrac{M}{nF} \cdot It$	Faraday 1st law
$\dfrac{m_1}{m_2} = \dfrac{E_1}{E_2}$	Faraday 2nd law
$\Lambda_m = \dfrac{\kappa \times 1000}{C}$	molar conductance
$\Lambda_m^\infty = \sum \nu_+ \lambda_+ + \sum \nu_- \lambda_-$	Kohlrausch's law
$\alpha = \dfrac{\Lambda_m}{\Lambda_m^\infty}$	degree of dissociation
$E^\circ = \dfrac{0.0592}{n} \log K_c$	equilibrium link

Faraday's Law — Numerical Variations (PYQ)

Q1 (PYQ W'25): Find time

How long must 2 A current pass to deposit 1.27 g of copper? ($Z_{Cu} = 3.29 \times 10^{-4}$ g/C)

$$t = \frac{m}{Z \cdot I} = \frac{1.27}{3.29 \times 10^{-4} \times 2}$$

$$\boxed{t = 1930\,\text{s} \approx 32.2\,\text{min}}$$

Q2 (PYQ Su'25): Find current

What current deposits 5.4 g Ag in 1 hour? ($M_{Ag} = 108$, $n = 1$)

$$I = \frac{m \cdot n \cdot F}{M \cdot t} = \frac{5.4 \times 1 \times 96500}{108 \times 3600}$$

$$\boxed{I = 1.34\,\text{A}}$$

Selective Electrode Reactions in Electrolysis

Why Some Ions Discharge First?

When several ions are present, the **ease of discharge** follows electrochemical series:

- At cathode: ion with **higher reduction potential** discharges first
- At anode: ion requiring **least energy** to oxidize discharges first

Example: Electrolysis of $CuSO_4$ with Pt electrodes

Cathode: Cu^{2+} ($+0.34$ V) discharges before H^+ (0.00 V)
$Cu^{2+} + 2e^- \rightarrow Cu$ (deposits)

Anode: OH^- discharges before SO_4^{2-} (very stable)
$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Batteries — Primary vs Secondary

Primary Battery

Non-rechargeable. Reactions irreversible.

Type	**EMF**
Dry cell	1.5 V
Alkaline	1.5 V
Mercury	1.35 V
Zinc-air	1.4 V

Secondary Battery

Rechargeable. Reactions reversible.

Type	**EMF**
Lead-acid	2 V/cell
Ni-Cd	1.25 V
Ni-MH	1.2 V
Li-ion	3.6 V

Lead-acid (car battery) $= 6$ cells $\times$ 2 V $=$ 12 V

Lead-Acid Battery (Secondary Battery)

Construction

Anode: spongy Pb Cathode: PbO_2 Electrolyte: H_2SO_4 ($d = 1.28$ g/mL)

Discharge Reactions

Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
Overall: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

Recharging

Reverse reactions occur. $PbSO_4 \rightarrow Pb$ and PbO_2. Acid density increases on charging (H_2SO_4 regenerated).

Fuel Cells

Definition

A device that **continuously converts chemical energy** of a fuel directly to electrical energy as long as fuel and oxidant are supplied. Efficiency $\approx 70\%$ vs thermal 30–40%.

H_2–O_2 Fuel Cell

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Overall: $2H_2 + O_2 \rightarrow 2H_2O$

Advantages

- No pollution (product: H_2O)
- High efficiency
- No moving parts
- Continuous operation
- Used in space vehicles

Galvanic vs Electrolytic Cell — Detailed Comparison

Feature	Galvanic Cell	Electrolytic Cell
Energy conversion	Chemical→Electrical	Electrical→Chemical
Spontaneity	Spontaneous	Non-spontaneous
Anode sign	Negative $(-)$	Positive $(+)$
Cathode sign	Positive $(+)$	Negative $(-)$
External supply needed?	No (generates EMF)	Yes
Salt bridge	Required	Not required
Container setup	Two half-cells	Single container
Examples	Daniel cell, batteries	Plating, refining
ΔG	Negative	Positive

Key trick: Anode = oxidation in *both* types; only the charge sign flips.

Nernst Equation — Extended Numerical (PYQ Su'25)

Problem

Calculate EMF of: $\mathrm{Zn}\,|\,\mathrm{Zn^{2+}}(0.001\ \mathrm{M})\,||\,\mathrm{Cu^{2+}}(0.1\ \mathrm{M})\,|\,\mathrm{Cu}$

$E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.76\,\mathrm{V}, \quad E^\circ_{\mathrm{Cu^{2+}/Cu}} = +0.34\,\mathrm{V}$

Solution

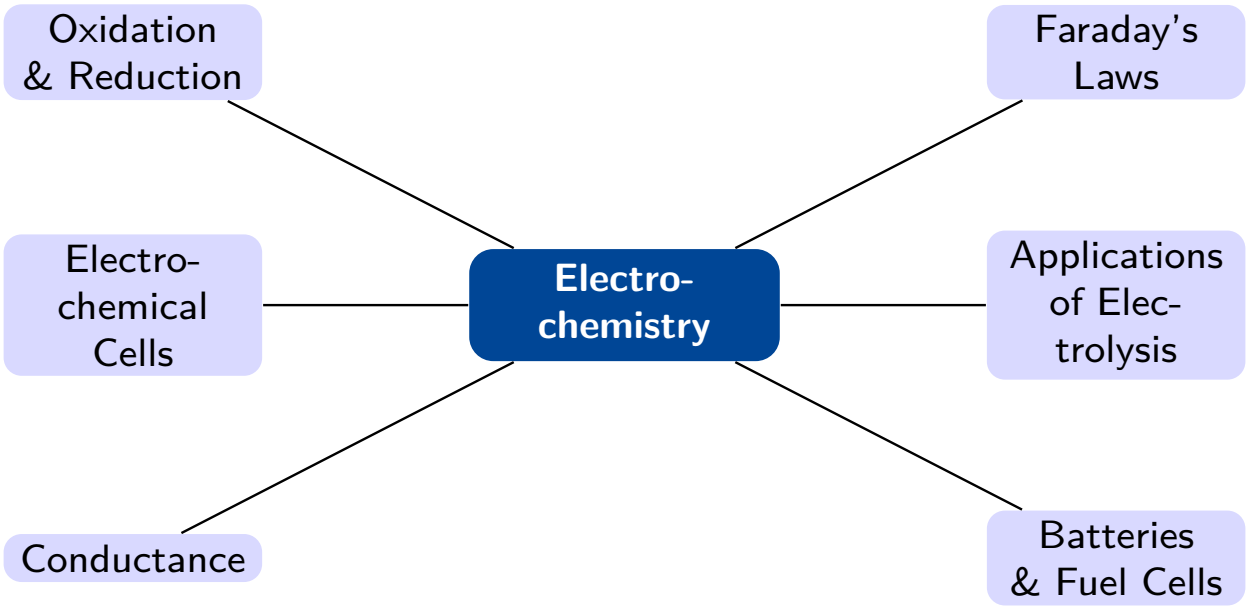
Step 1: $E^\circ_{\mathrm{cell}} = 0.34 - (-0.76) = 1.10\,\mathrm{V}$

Step 2: $Q = \dfrac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cu^{2+}}]} = \dfrac{0.001}{0.1} = 0.01; \quad n = 2$

Step 3: $E = 1.10 - \dfrac{0.0592}{2}\log(0.01) = 1.10 - 0.0296 \times (-2)$

$$\boxed{E = 1.10 + 0.059 = 1.159\,\mathrm{V}}$$

Unit 2 — Electrochemistry Mind Map



OIL RIG | Nernst | Daniel cell | SHE | Kohlrausch | $m = ZIt$ | Electroplating | Lead-acid

Exam Tips — Unit 2 Electrochemistry

Do's

- Write full half-reactions for both electrodes
- State Faraday's laws in words before formula
- Show units at every step in numericals
- Draw neat Daniel cell / electrolytic cell diagram
- Use OIL RIG for oxidation/reduction definition

Don'ts

- Don't confuse anode charge sign (galvanic vs electrolytic)
- Don't mix log and ln in Nernst
- Don't forget n in $Z = M/(nF)$
- Don't skip salt bridge explanation
- Don't say cathode = oxidation site (it's reduction!)

Quick recall: $m = ZIt$ | $E = E^\circ - \frac{0.0592}{n} \log Q$ | $\Delta G = -nFE^\circ$

PYQ Short-Answer Practice — 2 Marks

Frequently Asked 2-Mark Questions

#	Question
1	Define oxidation number. Find O.N. of Cr in $K_2Cr_2O_7$.
2	What is SHE? What is its electrode potential?
3	State Faraday's second law with formula.
4	Distinguish between specific and molar conductance.
5	What is electrochemical equivalent? Give its unit.
6	Define degree of dissociation and give formula.
7	What is salt bridge? State its two functions.
8	Explain OIL RIG with one example.
9	Write Nernst equation; define each term.
10	What are concentration cells? Give one example.

Specific & Molar Conductance Numerical (PYQ W'24)

Problem

Resistance of conductance cell filled with 0.1 M KCl = 100 Ω. Cell constant = $0.88\,\text{cm}^{-1}$.
Find (a) specific conductance and (b) molar conductance.

Solution

(a) $\kappa = \dfrac{\text{Cell constant}}{R} = \dfrac{0.88}{100} = 8.8 \times 10^{-3}\,\text{S cm}^{-1}$

(b) $\Lambda_m = \dfrac{\kappa \times 1000}{C} = \dfrac{8.8 \times 10^{-3} \times 1000}{0.1}$

$$\boxed{\Lambda_m = 88\,\text{S cm}^2\text{mol}^{-1}}$$

Units: κ in S/cm; C in mol/L; Λ_m in S·cm^2/mol

Galvanic Corrosion (Bridge to Unit 3)

Galvanic Corrosion

When two **dissimilar metals** are in electrical contact in an electrolyte, the more active metal (lower E°) becomes the anode and corrodes faster.

Fe–Cu Couple in Seawater

Anode: Fe (-0.44 V) oxidizes
Cathode: Cu ($+0.34$ V) protected

$\Rightarrow$ Iron rusts faster at junction

Prevention

- Use metals close in series
- Use insulating spacers
- Apply protective coatings
- Cathodic protection (Unit 3)

Unit 2 Revision Flash Points

Must Know Facts

- SHE potential $= 0.00$ V (by convention)
- 1 Faraday $= 96500$ C $=$ charge of 1 mol e^-
- Daniel cell: Zn anode, Cu cathode, $E^\circ = 1.10$ V
- Salt bridge: KCl/NH_4NO_3 in agar-agar
- Plating time $\propto$ mass; $\propto 1/\text{current}$
- Λ_m increases with dilution (weak electrolytes)

Common Exam Errors

- Writing anode as +ve in galvanic cell ✗
- Forgetting n in $Z = M/(nF)$
- Confusing κ (S/cm) with Λ_m
- Wrong Q in Nernst equation
- Saying cathode $=$ oxidation site ✗

Overpotential & Decomposition Potential

Decomposition Potential

The **minimum voltage** required to cause continuous electrolysis.
Water: theoretical = 1.23 V, actual $\approx$ 1.7 V (due to overpotential).

Overpotential

Extra voltage beyond the theoretical value due to:

- Electrode surface effects (especially for H_2 and O_2 evolution)
- Ohmic resistance of electrolyte
- Concentration polarization

Overpotential = Actual applied potential − Theoretical potential

H_2 overpotential is highest on smooth Pt, lowest on platinized Pt. Hence spongy/platinized electrodes are preferred.

Unit 2 Complete — Bridge to Unit 3: Corrosion

Unit 2 Summary

Topic	Core Outcome
Redox	OIL RIG; O.N. rules; cell reactions
Electrochemical cells	Daniel cell; Nernst; E°; SHE
Conductance	κ, Λ_m, Kohlrausch's law
Faraday's Laws	$m = ZIt$; 2nd law; numericals
Electrolysis	Plating, refining, brine, galvanizing
EMF & ΔG	$\Delta G = -nFE$; spontaneity
Batteries	Lead-acid; fuel cells; primary/secondary

Coming Next — Unit 3: Corrosion

Corrosion is **electrochemistry in action** on metal surfaces. Unit 3: dry vs wet corrosion, rusting mechanism, factors affecting corrosion, prevention by galvanizing, cathodic protection, inhibitors, and coatings.

Unit 3: Corrosion

Engineering Chemistry — DI01000071

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Unit 3 Syllabus Overview

Topics Covered

#	Topic
1	Definition & Significance of Corrosion
2	Types: Dry (Chemical) Corrosion
3	Types: Wet (Electrochemical) Corrosion
4	Mechanism of Rusting of Iron
5	Factors Affecting Corrosion
6	Prevention: Coatings (metallic, non-metallic)
7	Prevention: Galvanizing & Tinning
8	Prevention: Cathodic Protection
9	Prevention: Corrosion Inhibitors

Weightage: ≈12% of paper **PYQ:** 7-mark asked every exam

Definition & Significance of Corrosion

Definition

Corrosion is the gradual deterioration or destruction of metals by chemical or electrochemical reaction with the surrounding environment (atmosphere, moisture, or chemicals).

Examples

- Rusting of iron ($Fe_2O_3 \cdot xH_2O$)
- Tarnishing of silver (Ag_2S)
- Green patina on copper ($CuCO_3 \cdot Cu(OH)_2$)
- Dissolution of Zn in acid

Economic Significance

- Billions lost annually worldwide
- Structural failures (bridges, pipelines)
- Shortened equipment life
- India: $\approx$\$14 billion/year loss

Dry Corrosion

(Chemical Corrosion)

Dry (Chemical) Corrosion

Definition

Corrosion caused by the **direct chemical reaction** of metals with dry gases (O_2, CO_2, SO_2, halogens) — no moisture required; occurs at high temperatures.

Type	Agent	Product
Oxidation by O_2	Oxygen	Metal oxide
Oxidation by halogens	Cl_2, Br_2	Metal halide
Oxidation by SO_2	Sulphur dioxide	Metal sulphate
H_2 embrittlement	H_2	Metal hydride

Example Reactions

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$ (iron oxide at high temp.)
$Cu + Cl_2 \rightarrow CuCl_2$
$2Ag + H_2S \rightarrow Ag_2S + H_2$ (tarnishing)

Pilling-Bedworth (P-B) Ratio

Definition

$$P\text{-}B \text{ Ratio} = \frac{\text{Volume of metal oxide formed}}{\text{Volume of metal consumed}}$$

P-B < 1 (porous oxide)

Oxide layer **porous** $\Rightarrow$ does not protect.
Corrosion continues.
Example: Alkali metals (Na, K, Mg)

P-B ≈ 1 (protective)

Oxide layer **compact & adherent** $\Rightarrow$ protects.
Corrosion stops (passivation).
Example: Al (Al_2O_3), Cr, Ni

P-B > 2: Oxide flakes/cracks (not protective either) — e.g., Fe_2O_3 (scale at high temp.)

Wet Corrosion

(Electrochemical Corrosion)

Wet (Electrochemical) Corrosion

Definition

Corrosion occurring in presence of **moisture/electrolyte** by electrochemical mechanism. Metal acts as galvanic cell — different regions act as anode and cathode.

Requirements

1. Two dissimilar metals (or regions)
2. Electrolyte (moisture)
3. Electrical contact between them
4. Oxygen or H^+ (cathodic agent)

Anodic vs Cathodic

Anode (active metal):
$M \rightarrow M^{n+} + ne^-$ (oxidation)

Cathode (noble region):
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
or $2H^+ + 2e^- \rightarrow H_2 \uparrow$

Mechanism of Rusting of Iron (PYQ W'23, Su'24)

Step-by-Step Mechanism

Anodic reaction ($Fe \rightarrow Fe^{2+}$):

$$Fe - 2e^- \rightarrow Fe^{2+}$$

Cathodic reaction (O_2 reduction):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Formation of $Fe(OH)_2$:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

Oxidation to $Fe(OH)_3$ and dehydration:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O \textbf{ (Rust)}$$

Rust colour: Reddish-brown; loose, porous structure; no protection

Differential Aeration Corrosion

Principle

When different parts of the same metal are exposed to **different oxygen concentrations**, the part with **less O_2** becomes the anode and corrodes.

Mechanism

Less O_2 region (anode):
$Fe \rightarrow Fe^{2+} + 2e^-$

More O_2 region (cathode):
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Practical Example

Iron pipe partially buried in soil:

Underground (less O_2) $\rightarrow$ anode $\rightarrow$ corrodes

Above ground (more O_2) $\rightarrow$ cathode $\rightarrow$ protected

Also: Iron under rust pits vs open surface

Galvanic Corrosion

Principle

When two **dissimilar metals** are in electrical contact in an electrolyte, a galvanic cell forms. The **more active metal** (lower E°) acts as anode and corrodes faster.

Examples

Couple	Anode	Result
Fe–Cu	Fe (-0.44 V)	Fe corrodes near Cu joint
Zn–Fe	Zn (-0.76 V)	Zn corrodes, Fe protected
Al–Cu	Al (-1.66 V)	Al corrodes rapidly

Rule: Greater the potential difference between metals, faster the galvanic corrosion.

Waterline (Concentration Cell) Corrosion

Definition

Corrosion occurring at the **water–air interface** (waterline) due to **differential oxygen concentration** above vs below the waterline.

Mechanism

Below waterline: Less O_2 $\rightarrow$ anode $\rightarrow$ corrodes (pitting)

At/above waterline: More O_2 $\rightarrow$ cathode $\rightarrow$ rust deposits appear here

Observed in

- Ship hulls
- Water storage tanks
- Marine structures
- Bridge pillars in rivers

Note: Rust is deposited where O_2 is high; actual metal loss is below the waterline!

Factors Affecting Corrosion (PYQ Su'23, W'24)

Factor	Effect on Corrosion
Nature of metal	Active metals (high O.N., low E°) corrode faster
Purity of metal	Impure metals corrode faster (galvanic cells formed)
Physical state	Fine powder $>$ bulk; stressed metal corrodes faster at stress
Position in e-chem series	More active $=$ more corrosion tendency
pH of medium	Acidic medium accelerates corrosion
O_2 concentration	More $O_2 \rightarrow$ faster cathodic reaction
Temperature	Higher temp. accelerates rate
Humidity	More moisture $\rightarrow$ more electrolyte $\rightarrow$ faster wet corrosion
Presence of CO_2/SO_2	Makes water acidic; accelerates corrosion

Passivation

Definition

Passivation is the formation of a thin, adherent, compact, and impervious oxide film on a metal surface that **prevents further corrosion**.

Passive Metals

Metal	**Passive Film**
Aluminium	Al_2O_3
Chromium	Cr_2O_3
Nickel	NiO
Stainless steel	Cr_2O_3 layer
Titanium	TiO_2

Characteristics of Passive Film

- Thin (nanometres thick)
- Adherent — does not peel
- Impervious to gases/liquids
- Self-repairing (heals if scratched)
- P-B ratio ≈ 1

Corrosion Prevention — Overview

Methods of Corrosion Prevention

Category	Methods
Proper design	Avoid dissimilar metal contact; minimize crevices
Metallic coatings	Galvanizing, tinning, chromium plating, anodizing, electroplating
Non-metallic coatings	Painting, plastic/rubber lining, ceramic/enamel coating
Cathodic protection	Sacrificial anode, impressed current method
Inhibitors	Anodic, cathodic, mixed inhibitors (add to corrosive medium)
Alloying	Stainless steel (Fe+Cr+Ni), Monel metal (Ni+Cu)

Key principle: Break any one link of the corrosion chain (electrolyte, anode, cathode, or electrical contact).

Metallic Coatings (PYQ W'25, Su'24)

Types of Metallic Coatings

Method	Metal Used	Base Metal/Use
Galvanizing	Zinc	Iron/steel; roofing, pipes
Tinning	Tin	Iron (food cans, cookware)
Chrome plating	Chromium	Auto parts, tools
Nickel plating	Nickel	Base under chrome; sanitary
Copper plating	Copper	Printed circuits, decorative
Silvering	Silver	Cutlery, mirrors
Anodizing	Al_2O_3	Aluminium articles

Application Methods

Electroplating | **Hot-dip** | **Spraying** | **Cementation** | **Cladding**

Galvanizing (PYQ W'23, Su'24)

Definition

Coating of **zinc** on iron/steel to prevent rusting. Zinc is more active than iron ($E^\circ_{Zn} < E^\circ_{Fe}$), so zinc acts as sacrificial anode even if coating is scratched.

Process (Hot-Dip)

1. Clean iron: remove rust/scale with dilute H_2SO_4 (pickling)
2. Rinse with water; flux ($ZnCl_2$) treatment
3. Dip in molten zinc at 450 °C
4. Withdraw and cool; zinc–iron alloy interlayer forms

Uses: Roofing sheets, water pipes, buckets, nails, wire fence, corrugated iron sheets.

Tinning

Definition

Coating of **tin** on iron/steel. Tin ($E^\circ = +0.14$ V) is **less active** than iron (-0.44 V), so tin protects by **barrier action** only — if scratched, iron underneath corrodes faster.

Process

1. Clean iron (pickle with H_2SO_4)
2. Flux treatment ($ZnCl_2$)
3. Dip in molten tin (240 °C)
4. Squeeze through rollers for uniform coat

Applications & Comparison

Uses: Food cans, milk containers, kitchen utensils.

Tin is non-toxic and food-safe, hence preferred over Zn for food contact.

Galvanizing vs Tinning

Feature	Galvanizing	Tinning
Coating metal	Zinc (Zn)	Tin (Sn)
Position vs Fe	More active	Less active
Protection type	Sacrificial + barrier	Barrier only
If scratched	Zn corrodes, Fe safe	Fe corrodes faster
Food safe?	No (Zn toxic)	Yes (Sn non-toxic)
Application	Outdoor structures	Food containers
Process temp	$\approx 450\,^{\circ}\mathrm{C}$	$\approx 240\,^{\circ}\mathrm{C}$
Thickness	Thicker coat needed	Thinner coat sufficient

Key exam point: Galvanizing protects sacrificially; tinning only by barrier — if tinning is broken, corrosion is accelerated.

Non-Metallic Coatings

Organic Coatings

Type	Examples
Paints	Lead-based, oxide paints
Varnish	Alkyd, polyurethane
Lacquers	Nitrocellulose lacquer
Bituminous	Tar, asphalt (pipelines)
Plastic	PVC, polyethylene lining
Rubber	Vulcanized rubber lining

Inorganic Coatings

Type	Examples/Use
Enamel	Cookware, bath fittings
Ceramic	Furnaces, tiles
Cement	Underground pipes
Phosphating	Steel pre-treatment

Mechanism: Barrier between metal and environment; no electrochemical protection

Cathodic Protection

(Sacrificial Anode & Impressed Current)

Cathodic Protection (PYQ W'24, Su'25)

Principle

Make the metal to be protected the **cathode** of the electrochemical cell — cathode does not corrode (only oxidation/anode corrodes). Achieved by two methods:

1. Sacrificial Anode Method
2. Impressed Current Method (ICCP)

Where Used

- Underground pipelines (oil, gas, water)
- Ship hulls
- Marine structures (jetties, offshore platforms)
- Water storage tanks
- Concrete-embedded steel reinforcement

Sacrificial Anode Method (PYQ W'24, Su'24)

Principle

A more **active metal** (sacrificial anode) is electrically connected to the structure to be protected. The active metal corrodes preferentially, making the structure the cathode.

Anode Materials

Applied to	**Anode Used**
Iron structure	Zinc or Magnesium
Ship hull	Zinc blocks
Oil pipelines	Mg-alloy

Features

- No external power needed
- Simple installation
- Anodes must be replaced periodically
- Economical for small structures

Impressed Current Cathodic Protection (ICCP)

Principle

An **external DC source** is connected with its **negative terminal to the structure** (making it cathode) and positive to an **inert anode** (scrap iron, graphite, platinum) buried nearby.

Advantages

- External current can be adjusted
- Inert anode lasts longer
- Economical for large structures (pipelines >100 km)
- Effective in any soil/water

Setup

DC Source (+ve) $\rightarrow$ inert anode (in ground)
DC Source (−ve) $\rightarrow$ pipeline/structure
Current flows; structure becomes cathode; no corrosion.

Sacrificial Anode vs ICCP

Feature	Sacrificial Anode	ICCP
External power	Not required	Required (DC source)
Anode material	Active metal (Zn/Mg)	Inert (graphite/Pt)
Cost	Low initial cost	Higher initial cost
Maintenance	Replace anodes periodically	Monitor current levels
Scale of use	Small structures	Large pipelines, ships
Current control	None	Adjustable
Risk of overprotection	No	Yes (H embrittlement)

Both methods make the metal the cathode — this is the unifying principle.

Corrosion Inhibitors (PYQ W'23, W'25)

Definition

Substances added in **small amounts** to the corrosive medium that **significantly reduce the corrosion rate** without changing the properties of the medium.

Type	Mechanism	Examples
Anodic inhibitor	Forms oxide passive film on anode	Na_2CrO_4, $NaNO_2$, NaOH
Cathodic inhibitor	Precipitates on cathode; blocks O_2 reduction	$ZnSO_4$, $CaCO_3$, $MgSO_4$
Mixed inhibitor	Acts on both electrodes	Phosphates, silicates, amines
Organic inhibitor	Adsorbs on metal surface; forms protective film	Amines, mercaptans, thiourea

Application: Cooling water systems, acid pickling baths, oil/gas pipelines

Alloying for Corrosion Resistance

Why Alloying Helps

Adding **alloying elements** that form a stable, adherent oxide layer on the metal surface provides corrosion resistance by passivation.

Alloy	Composition	Property
Stainless steel (304)	Fe + 18% Cr + 8% Ni	Cr_2O_3 passive layer
Stainless steel (316)	+ 2% Mo	Resistant to Cl^-
Aluminium alloys	Al + Mg/Cu/Si	Al_2O_3 passive layer
Monel metal	67% Ni + 33% Cu	Seawater resistant
Inconel	Ni + Cr + Fe	High-temp. resistance
Cupronickel	Cu + Ni	Marine applications

Minimum 12% Cr needed in stainless steel for effective passivation (Cr_2O_3 layer)

Corrosion in Specific Environments

Atmospheric Corrosion

Humidity	>60% RH accelerates
SO_2	Forms H_2SO_4; attacks
CO_2	Mild acidification
NaCl (marine)	Electrolyte; aggressive

Soil Corrosion

Factors: moisture, pH, aeration, salt content, SRB bacteria (anaerobic)

Marine Corrosion

Seawater: high NaCl + dissolved O_2 = aggressive electrolyte.

Splash zone: Most aggressive (O_2 high, wet)
Tidal zone: Differential aeration
Underwater: Biological fouling

Used: Cathodic protection + anti-corrosion paints (epoxy-zinc primer) for ships

PYQ 7-Mark Questions — Corrosion (Unit 3)

Frequently Asked Long Questions

Question	Papers
Explain mechanism of rusting of iron	W'23, Su'24
Explain sacrificial anode method with diagram	W'24, Su'24
Describe cathodic protection (impressed current)	Su'25, W'25
What is galvanizing? Explain process and uses	W'23, Su'24
Compare galvanizing and tinning	Su'23, W'24
What are corrosion inhibitors? Types and examples	W'23, W'25
Explain electrochemical (wet) corrosion mechanism	Su'24, W'25

Strategy

Every 7-mark corrosion answer needs: definition + mechanism (reactions) + diagram + examples + comparison or application

Unit 3 Mid-Point Summary

Topic	Key Points
Definition	Deterioration by chemical/electrochemical reaction
Dry corrosion	Direct reaction with gases; P-B ratio; passivation
Wet corrosion	Electrolyte needed; anode corrodes; OIL RIG
Rusting	4-step: $Fe^{2+} \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow$ rust
Galvanic corrosion	Dissimilar metals; active one corrodes
Diff. aeration	Less O_2 = anode; more O_2 = cathode
Prevention	Coatings | Galvanizing | Tinning | Inhibitors | CP
Cathodic protection	Sacrificial anode or impressed current (ICCP)

Stress Corrosion Cracking (SCC)

Definition

Cracking caused by the **combined action of tensile stress** (residual or applied) and a **specific corrosive environment**. Metal fails at stress much lower than yield strength.

Examples

Metal	**Environment**
Brass	NH_3 (season cracking)
Stainless steel	Cl^- ions (seawater)
Al alloys	$NaCl + H_2O$
Steel	NaOH (caustic SCC)

Prevention

- Stress relief annealing
- Reduce Cl^- concentration
- Use SCC-resistant alloys
- Cathodic protection
- Shot peening (compressive stress)

Pitting Corrosion

Definition

Localized corrosion that produces small pits or holes on the metal surface. Very dangerous — deep pits cause structural failure with little visible surface damage.

Mechanism

1. Passive film breaks at a point (scratch or Cl^- attack)
2. Small exposed area becomes **anode** (concentrated corrosion)
3. Large passive area = **cathode** (small anode:cathode ratio)
4. Pit deepens rapidly; autocatalytic process

Critical factor: Chloride ions (Cl^-) break passive films on stainless steel, Al, Ti. Marine environments are high risk.

Crevice Corrosion

Definition

Corrosion occurring in **narrow gaps** (crevices) between metal surfaces or between metal and non-metal — bolts, gaskets, riveted joints, lap joints.

Mechanism

Inside crevice: O_2 depleted $\rightarrow$ anode
Outside: O_2 rich $\rightarrow$ cathode
Self-accelerating — pH drops inside crevice (Cl^- accumulates)

Prevention

- Seal crevices with weld/sealant
- Use non-absorbent gaskets
- Design to allow drainage
- Use Cl^--resistant alloys (316 SS)

Hydrogen Embrittlement

Definition

The absorption of atomic hydrogen into metals during corrosion or electroplating, making them **brittle and prone to cracking** under stress.

How It Occurs

- Atomic H (not H_2) enters metal lattice
- H accumulates at defects/grain boundaries
- Internal pressure builds $\rightarrow$ cracks
- Most common in high-strength steels

Prevention

- Bake after electroplating (200 °C, 12 hr)
- Use low-hydrogen welding electrodes
- Apply hydrogen barrier coatings
- Avoid overprotection in cathodic protection (ICCP risk)

Painting as Corrosion Prevention

Principle

Paint forms a **physical barrier** between metal and corrosive environment. Effective only when paint film is **intact and adherent**.

Paint System Layers

Layer	Purpose
1. Surface preparation	Sand-blast / phosphate treatment
2. Primer	Adhesion + anti-corrosion (zinc-rich, red oxide)
3. Undercoat	Build film thickness
4. Topcoat	Weather/UV resistance; decorative

Zinc-rich primers have Zn particles that provide sacrificial protection even under the paint film.

Phosphating & Chromating (Surface Treatments)

Phosphating

Steel is treated with **phosphoric acid solution** $\rightarrow$ forms insoluble zinc/iron phosphate layer on surface.

Type	Zinc phosphate, Iron phosphate
Basis	Adherent, porous layer
Use	Pre-treatment before painting; i

Chromating (Passivation)

Metal treated with chromic acid/chromate salts $\rightarrow$ forms Cr(III) oxide passive film.

Used on	Al, Zn, Mg alloys
Result	Adherent Cr_2O_3 film
Use	Aerospace, auto industry

Note: Hexavalent Cr (Cr^{6+}) is toxic; Cr^{3+}-based alternatives used.

Corrosion Resistance of Common Metals

Metal	Why Resistant	Environment	Weak vs.
Aluminium	Al_2O_3 passive layer	Air, weak acid	HCl, NaOH
Chromium	Cr_2O_3 film	Air, oxidizing acid	HCl, H_2SO_4
Nickel	NiO film	Many environments	Oxidizing acids
Titanium	TiO_2 film (very stable)	Seawater, acids	HF
Stainless steel	Cr_2O_3 (12%+ Cr)	Air, water, mild acids	Cl^-, HCl
Gold/Platinum	Noble (high E°)	Almost all	Aqua regia
Zinc	$ZnO/Zn(OH)_2$ (slight)	Air, neutral water	Acids, alkalis

Biocorrosion (Microbiologically Influenced Corrosion)

Definition

Corrosion caused or accelerated by microorganisms (bacteria, fungi) in the surrounding environment. Common in soils, marine environments, and water systems.

Organisms

SRB: Sulfate-reducing bacteria
$SO_4^{2-} \rightarrow H_2S$ (attacks iron)

IOB: Iron oxidizing bacteria
Oxidize $Fe^{2+} \rightarrow Fe^{3+}$ (pitting)

Prevention

- Biocides in water systems
- Protective coatings
- Cathodic protection
- Pipe pigging (physical cleaning)
- Sterile soil backfill

Unit 3 PYQ Pattern Analysis

Topic	Su'23	W'23	Su'24	W'24	Su'25/W'25
Rusting mechanism	2	7	7	2	2
Cathodic protection	2	2	2	7	7
Galvanizing	7	7	7	2	2
Tinning	2	2	2	2	2
Galvanizing vs Tinning	7	2	2	7	2
Corrosion inhibitors	2	7	2	2	7
Wet corrosion	2	2	7	2	7
Dry corrosion / P-B ratio	2	2	2	2	2
Factors affecting	2	2	2	7	2

High probability 7-mark: Rusting mechanism + Cathodic protection + Galvanizing

Corrosion Numerical — Weight Loss Calculation

Corrosion Rate Expressed as

mpy (mils per year): $\text{mpy} = \dfrac{534 \times W}{D \times A \times T}$

Where: W = weight loss (mg), D = density (g/cm^3), A = area (in^2), T = time (hr)

Or simply: **corrosion rate** $= \dfrac{\text{mass loss}}{\text{area} \times \text{time}}$ $\quad (\text{mg cm}^{-2}\ \text{hr}^{-1})$

Example

Iron plate (area $= 10\,\text{cm}^2$) loses $0.5\,\text{mg}$ in 2 hours.

Corrosion rate $= \dfrac{0.5}{10 \times 2} = \mathbf{0.025}\,\text{mg cm}^{-2}\text{h}^{-1}$

PYQ Short-Answer Practice — Unit 3 (2 Marks)

Common 2-Mark Questions

#	Question
1	Define corrosion. Give two examples.
2	What is dry corrosion? Give one example with reaction.
3	Define Pilling-Bedworth ratio. What does P-B < 1 indicate?
4	What is passivation? Name two passive metals.
5	Distinguish between galvanizing and tinning.
6	What is a sacrificial anode? Name two metals used.
7	Define differential aeration corrosion. Give one example.
8	What is pitting corrosion? Why is it dangerous?
9	Name two types of corrosion inhibitors with examples.
10	What is stress corrosion cracking?

Exam Tips — Unit 3 Corrosion

Do's

- Write all 4 steps of rusting mechanism with chemical equations
- Clearly label anode/cathode in cathodic protection diagram
- State P-B ratio with all three cases
- Distinguish galvanizing vs tinning in a table
- Mention that inhibitors are added in small amounts

Don'ts

- Don't say tinning protects sacrificially (it doesn't!)
- Don't skip the oxidation reaction in wet corrosion
- Don't mix cathodic protection with cathodic inhibitors
- Don't forget that ICCP uses a DC source
- Don't confuse galvanizing (Zn) with chromium plating

Unit 3 Revision Flash Points

Must Know Facts

- Rusting: Fe $\rightarrow$ rust (4 reactions)
- P-B ratio: <1 = porous; ≈ 1 = protective
- Galvanizing temp: $\approx 450\,^{\circ}\text{C}$ (hot-dip Zn)
- Tinning temp: $\approx 240\,^{\circ}\text{C}$ (hot-dip Sn)
- Sacrificial anodes: Zn, Mg (for Fe structures)
- Stainless steel: min 12% Cr for corrosion resistance
- ICCP: negative terminal to structure

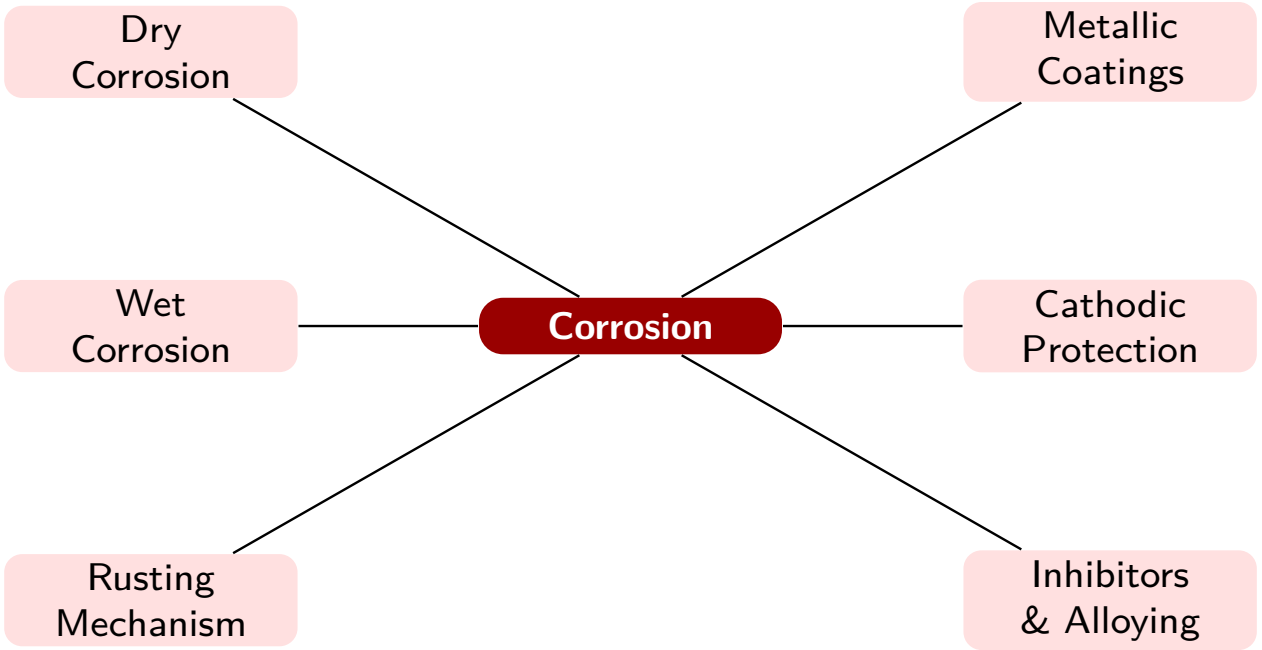
Quick Comparison

Anode	Corrodes (oxidation)
Cathode	Protected (reduction)
Zn on Fe	Sacrificial (active E°)
Sn on Fe	Barrier only (noble E°)
Dry corrosion	No moisture
Wet corrosion	Electrochemical

Unit 3 Key Summary Table

Topic	Core Content
Dry corrosion	Direct rxn with O_2/halogens/SO_2; P-B ratio
Wet corrosion	Electrochemical; anode oxidizes; cathode protected
Rusting	$Fe \rightarrow Fe^{2+} \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow$ rust
Galvanic corrosion	Dissimilar metals + electrolyte; active metal = anode
Diff. aeration	Less O_2 = anode; more O_2 = cathode
Galvanizing	Zn on Fe; sacrificial; 450°C hot-dip
Tinning	Sn on Fe; barrier only; 240°C; food-safe
Cathodic protection	Sacrificial anode (Zn/Mg) or ICCP (DC supply)
Inhibitors	Anodic (chromate) / Cathodic ($ZnSO_4$) / Mixed
Passivation	Adherent P-B≈1 oxide film (Al_2O_3, Cr_2O_3)

Unit 3 — Corrosion Mind Map



P-B ratio | OIL RIG | Galvanizing | Tinning | Sacrificial anode | ICCP

High-Temperature (Elevated Temp.) Corrosion

Definition

Corrosion of metals at **elevated temperatures** ($>300^\circ C$) by direct reaction with gases (O_2, SO_2, steam, fuel combustion products). Also called **oxidation corrosion** or **scaling**.

Reactions

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$ (scale)
$Ni + SO_2 \rightarrow NiO + S$
$2Cu + O_2 \rightarrow 2CuO$ (black scale)

Prevention

- Use high Cr/Ni alloys (Inconel, stainless)
- Protective coatings (aluminizing, chromizing)
- Ceramic coatings for furnace parts
- Control furnace atmosphere (reducing or inert)

Effect of pH on Corrosion

pH vs Corrosion Rate

pH	Effect on Iron Corrosion
< 4 (acidic)	Dissolution: $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$ (very fast; protective film dissolves)
4–10 (near neutral)	Moderate; $Fe(OH)_2$ forms; rate depends on O_2 access
> 10 (alkaline)	Passivation (stable Fe_2O_3 film); corrosion slows
Highly alkaline (>14)	Fe dissolves as $HFeO_2^-$ (amphoteric); corrosion again

Practical note: Concrete (pH $\approx$12) protects embedded steel by making it passive — but carbonation (CO_2 lowers pH) can cause depassivation and rebar corrosion.

Corrosion of Steel in Concrete (RCC)

Why Steel is Protected in Fresh Concrete

Fresh concrete is alkaline (pH ≈12–13). This causes steel reinforcement to form a **passive oxide film** that prevents corrosion.

Why Corrosion Starts in RCC

Carbonation: $CO_2 + H_2O \rightarrow H_2CO_3$ lowers pH below 9 $\Rightarrow$ passive film destroyed

Chloride ingress: Cl^- (from seawater or deicing salts) breaks passive film locally $\Rightarrow$ pitting corrosion

Prevention: Dense concrete (low w/c ratio) | Epoxy-coated rebars | Cathodic protection | Stainless steel rebars

Corrosion in Chemical Industry

Environment	Corrosive Agent	Material Used
Sulfuric acid	Conc. H_2SO_4	Lead, SS 316, glass-lined
Hydrochloric acid	HCl (dilute)	Rubber/plastic lining, Hastalloy
Alkali services	NaOH	Nickel, SS 304
Seawater	NaCl + O_2	Cupronickel, Ti, SS 316
Oxidizing acids	HNO_3	Stainless steel (passive)
High-temp gas	O_2, SO_2	Inconel, Incoloy
H_2S environment	Wet H_2S	Hard but ductile grades

Key principle: Match material to environment — no single metal resists all corrosive conditions.

Design Considerations for Corrosion Control

Engineering Design Rules

- **Avoid galvanic couples:** Use metals close in series, or insulate joints
- **Eliminate crevices:** Seal joints; use butt welds instead of lap welds
- **Allow drainage:** No pockets where water collects; incline surfaces
- **Minimize stress concentrations:** Smooth surfaces; avoid sharp corners
- **Accessibility:** Design for inspection, maintenance, and coating replacement
- **Material selection:** Use corrosion-resistant alloys in aggressive zones

Electrochemical Basis of Corrosion Control

Evans Diagram (Qualitative)

The corrosion potential and current are set by the intersection of anodic (oxidation) and cathodic (reduction) polarization curves. Methods to reduce corrosion current:

Method	Effect on Evans Diagram
Anodic inhibitor	Shifts anodic curve to lower current (passivates anode)
Cathodic protection	Shifts cathode potential below corrosion potential
Coatings	Remove electrode from electrolyte (no circuit)
Sacrificial anode	Provides anodic current from the anode (Zn/Mg), not the structure
ICCP	Applies cathodic current equal to corrosion current

Notable Corrosion Failures (Real Engineering Cases)

Why Study Corrosion Failures?

Corrosion failures cause loss of life, environmental damage, and economic losses. Understanding them guides prevention.

Case	Corrosion Type	Lesson
Aloha Airlines (1988)	Fatigue + pitting (Cl^-)	Inspect aging aircraft
Corroded Pt. Pleasant Bridge (1967)	SCC in wires	Avoid high-stress + hostile env.
Alaskan oil pipeline	Differential aeration	Cathodic protection + coatings
Statue of Liberty copper	Galvanic (Cu-Fe frame)	Isolation between metals
Petrobras P-36 (2001)	Crevice corrosion	Regular inspection of welds

Corrosion Monitoring Techniques

Electrochemical Methods

Method	**Principle**
LPR	Linear polarization r
EIS	Electrochemical imp
Potentiodynamic	Polarization scan
ZRA	Zero resistance amme

Non-Electrochemical Methods

Coupon test	Weight loss measur
UT	Ultrasonic thickness
RT/XT	X-ray/neutron testi
Acoustic emission	Crack detection

Simplest lab method: Coupon (test) specimens of known area immersed in corrosive solution for fixed time; weigh before/after.

Economic Impact of Corrosion

Global and National Statistics

Global annual cost	≈\$2.5 trillion (3.4% of global GDP)
USA	≈\$270 billion/year
India	≈\$14–20 billion/year
Industries affected	Oil/gas, infrastructure, aerospace, marine

Preventable Costs?

Studies suggest **25–40%** of corrosion costs are preventable with existing knowledge and technology — problem is implementation and maintenance.

Prevention Value

Every \$1 spent on corrosion prevention saves \$7–\$10 in repair/replacement costs.

Corrosion Behaviour: Aluminium vs Iron

Feature	Aluminium	Iron
Thermodynamic tendency	More reactive ($E^\circ = -1.66$ V)	Less reactive ($E^\circ = -0.44$ V)
Actual corrosion rate	Very slow (passive)	Moderate to fast
Oxide formed	Al_2O_3 (compact, P-B$\approx$1.3)	Fe_2O_3 (flaky, P-B$>$2)
Oxide property	Adherent, impervious, self-sealing	Loose (rust), porous
Net protection	Very good	Poor (rusts through)
Use in corrosive env.	Aircraft, marine, cookware	Needs coatings/protection

Key insight: Thermodynamic reactivity $\neq$ corrosion rate; kinetics (passive film) can override thermodynamics.

Corrosion and Environmental Pollution

Acid Rain and Corrosion

$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow H_2SO_4$ (acid rain, pH 4–5)
$NO_x + H_2O \rightarrow HNO_3$

Acid rain attacks: metals, limestone buildings, marble monuments, concrete

Tarnishing of Monuments

Material	**Effect**
Limestone/Marble	$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$
Bronze (Cu-Sn)	Green patina: $Cu_2(OH)_2CO_3$
Iron structures	Rust, pitting, loss of cross-section

Electroplating vs Galvanizing vs Tinning

Feature	Electroplating	Galvanizing	Tinning
Method	Electrolytic	Hot-dip (or electro)	Hot-dip
Coating metal	Any metal	Zinc	Tin
Thickness control	Very precise	Variable	Variable
Adhesion	Excellent	Good	Good
Alloy layer formed?	No	Yes (Zn-Fe)	Yes (Sn-Fe)
Sacrificial?	Depends on metal	Yes (Zn is active)	No (Sn is noble)
Food safe?	Depends	No	Yes
Cost	Higher per unit	Low (bulk)	Low (bulk)

Selecting the Right Corrosion Prevention Method

Decision Framework

Situation	Recommended Method
Outdoor structural steel	Galvanizing + epoxy primer
Food processing equipment	Stainless steel (316) or tinning
Underground pipeline	ICCP + polyethylene wrapping
Ship hull	Cathodic protection + anti-fouling paint
Electrical components	Nickel/gold electroplating
Boilers/pipes (water)	Anodic inhibitors (chromate, nitrite)
High-temp furnace parts	Ceramic/aluminide coating

Unit 3 — Formula & Data Summary

Key Formulas and Values

Formula/Value	Note
P-B Ratio $= V_{\text{oxide}}/V_{\text{metal}}$	< 1 porous; ≈ 1 protective
Corrosion rate = mass loss / (area $\times$ time)	$\text{mg/cm}^2\text{/hr}$
Rusting: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	Anodic reaction
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	Cathodic (neutral)
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	Cathodic (acidic)
Galvanizing temp	$\approx 450\,^\circ\text{C}$
Tinning temp	$\approx 240\,^\circ\text{C}$
Stainless steel Cr content	Min 12% for passivation

Unit 3 Complete — Bridge to Unit 4: Fuels

Unit 3 Summary

Topic	Core Outcome
Dry corrosion	Gases attack directly; P-B ratio; passivation
Wet corrosion	Electrochemical; 4 types of corrosion cells
Rusting	4-step mechanism; anode(Fe) + cathode(O_2)
Galvanizing	Zn sacrificial coating; hot-dip 450°C
Tinning	Sn barrier coating; 240°C; food-safe
Cathodic protection	Sacrificial anode (Zn/Mg) or ICCP
Inhibitors	Anodic / cathodic / mixed / organic

Coming Next — Unit 4: Fuels

Unit 4 covers **classification of fuels**, calorific values, Dulong's formula, solid/liquid/gaseous fuels, and combustion analysis.

Unit 4: Fuels

Engineering Chemistry — DI01000071

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Unit 4 covers the chemistry of fuels — their classification, calorific value, analysis, and types of solid/liquid/gaseous fuels. Topics include Dulong's formula, coal analysis, petroleum fractions, and combustion calculations.

Unit 4 — Topics and Weightage

Topics at a Glance

#	Topic	Key Concepts
1	Classification of Fuels	Natural, artificial, solid/liquid/gas
2	Calorific Value	GCV, NCV, formula
3	Dulong's Formula	Calculation of GCV from composition
4	Solid Fuels: Coal	Types, proximate, ultimate analysis
5	Coal Products	Coke, coal gas, coal tar
6	Petroleum	Origin, fractions, cracking
7	Gaseous Fuels	Natural gas, LPG, water gas, producer gas
8	Combustion	Air/fuel ratio, flue gas analysis
9	Numericals	GCV, NCV, Dulong, combustion air

Weightage: $\approx$14% | GTU pattern: 2 $\times$ 7-mark + short answers

Fuels — Definition and Classification

Definition

A **fuel** is any substance which, when burned in air (O_2), produces heat energy economically, without harmful products in large quantities.

Basis	Type	Examples
Origin	Natural	Wood, coal, natural gas, petroleum
Origin	Artificial/Derived	Coke, LPG, coal gas, diesel
State	Solid	Wood, coal, coke, peat, charcoal
State	Liquid	Petrol, diesel, kerosene, ethanol
State	Gas	Natural gas, LPG, producer gas
Application	Primary	Used as obtained from nature
Application	Secondary	Processed/derived from primary

Calorific Value (CV)

Definition

Calorific value: Heat released per unit mass/volume of a fuel on complete combustion.

Units: kJ/kg (solid/liquid) kJ/m^3 (gaseous fuels)

GCV (HCV)

Gross Calorific Value (Higher CV)
Heat evolved when all combustion products including water are condensed to liquid.

NCV (LCV)

Net Calorific Value (Lower CV)
Heat evolved when water in combustion products remains as steam (not condensed).

$\text{NCV} = \text{GCV} - 2442 \times m_w$ where m_w = mass of water formed per kg of fuel (kg/kg)

GCV–NCV Relationship and Formula

Relationship

NCV = GCV − latent heat of steam formed

If H = mass fraction of hydrogen in fuel:

Water formed per kg fuel = $9H$ kg

Latent heat of steam = 2442 kJ/kg (at 15°C)

$$\boxed{\text{NCV} = \text{GCV} - 9H \times 2442} \quad \text{(all in kJ/kg)}$$

Solved Example

A fuel has 15% H. GCV = 48000 kJ/kg. Find NCV.

Water = $9 \times 0.15 = 1.35$ kg

Latent heat = $1.35 \times 2442 = 3297$ kJ

NCV = $48000 - 3297 =$ **44703 kJ/kg**

Dulong's Formula for GCV

Dulong's Formula

$$\text{GCV} = 33800\,C + 144000\left(H - \frac{O}{8}\right) + 9390\,S \quad \text{kJ/kg}$$

where C, H, O, S = mass fractions (from ultimate analysis)

Explanation of Terms

$33800\,C$	Heat from combustion of carbon
$144000(H - O/8)$	Net heat from H (subtracting H already combined with O and not available for burning)
$9390\,S$	Heat from combustion of sulfur

Dulong's Formula — Solved Numerical

Problem Statement

Coal: C = 75%, H = 5%, O = 12%, S = 2%, N = 3%, Ash = 3%.
Find GCV and NCV. (Latent heat of steam = 2442 kJ/kg)

Solution

Using Dulong's formula:

$$\text{GCV} = 33800(0.75) + 144000\left(0.05 - \frac{0.12}{8}\right) + 9390(0.02)$$

$$= 25350 + 144000(0.05 - 0.015) + 187.8$$

$$= 25350 + 5040 + 187.8 = \mathbf{30577.8\ kJ/kg}$$

Water formed $= 9 \times 0.05 = 0.45$ kg

$\text{NCV} = 30577.8 - 0.45 \times 2442 = 30577.8 - 1098.9 = \mathbf{29478.9\ kJ/kg}$

Solid Fuels — Coal: Formation and Types

Formation of Coal (Coalification)

Buried plant material undergoes slow compression + chemical change over millions of years under high pressure and temperature.

Peat → **Lignite** → **Sub-bituminous** → **Bituminous** → **Anthracite**

Type	C %	GCV kJ/kg	Properties
Peat	60	15000	Youngest; high moisture
Lignite	65–70	20000	Brown coal; soft
Bituminous	75–85	32000	Most common; caking
Anthracite	92–95	36000	Hardest; highest C; least smoke

Proximate Analysis of Coal

What is Proximate Analysis?

Routine test to determine **moisture**, **volatile matter**, **ash**, and **fixed carbon** content (all in %) by simple heating tests.

Parameter	Method	Significance
Moisture	Heat at 110°C for 1h	Reduces GCV; transport problem
Volatile matter	950°C in closed crucible	Determines smoke, ease of ignition
Ash	700°C in open crucible	Residue; reduces efficiency
Fixed carbon	100 - (M + VM + Ash)	Main heat-giving component

Good coal: High fixed carbon, low moisture, low ash, moderate volatile matter

Ultimate Analysis of Coal

What is Ultimate Analysis?

Chemical (elemental) analysis of coal to determine **C, H, N, S, O, Ash** by specialized analytical methods. Used to calculate GCV using Dulong's formula.

Element	Typical %	Significance
C	50–95%	Primary heat-producing element
H	2–6%	High heat; contributes to NCV loss
S	0.5–3%	Causes acid rain, equipment corrosion
N	1–3%	Gas fuel only; NO_x on combustion
O	2–20%	Reduces effective H; reduces GCV
Ash	2–25%	Inert; handling/disposal problem

Proximate vs Ultimate Analysis

Feature	Proximate	Ultimate
What is determined	M, VM, Ash, FC	C, H, N, S, O, Ash
Apparatus	Muffle furnace	Specialized analyzers
Time required	Few hours	More time
Cost	Low	High
Use	Routine quality control	GCV calculation, detailed study
Gives GCV directly?	No	Yes (Dulong's formula)

GTU Exam tip: Both types are 7-mark questions. Proximate: explain each *step+calculation*. Ultimate: explain *each element significance + Dulong formula*.

Coal Products — Carbonization

What is Carbonization?

Carbonization: Destructive distillation of coal in the *absence of air* to give coke, coal tar, and coal gas.

LTC (Low-Temp, 500–700°C)

- Soft coke (smokeless domestic fuel)
- More tar (more light oil)
- Less gas

HTC (High-Temp, 900–1200°C)

- Hard coke (metallurgical)
- More gas (coal gas)
- Less tar (more heavy oil)

Products: **Coke** (solid) + **Coal tar** (liquid, for chemicals) + **Coal gas** (fuel gas) + **Ammonia liquor**

Coke — Properties and Uses

Coke Properties

Coke is the solid residue left after carbonization. It is mainly carbon (90–95%) with very low volatile matter.

Properties

- Grey, porous, hard
- High carbon content ($\sim$92%)
- Low moisture, low ash
- GCV $\approx$ 29000–33000 kJ/kg
- Burns without smoke (low VM)

Uses

- **Metallurgy:** Blast furnace (iron making)
- **Fuel:** Household heating
- **Reducing agent:** Metal extraction
- **Electrode manufacture:** Graphite electrodes

Coal Gas — Composition and Uses

What is Coal Gas?

Gas produced as byproduct of HTC of coal. *Calorific value* $\approx$ *20000 kJ/m*^{3}

Composition

Component	**Approx %**
H_2	50–54%
CH_4	30–35%
CO	6–8%
CnHm	2–4%
N_2, CO_2	Balance

Uses

- Domestic/industrial fuel
- Formerly used as town gas in pipelines
- Chemical feedstock (H_2)
- WARNING: Toxic (contains CO)

Petroleum — Origin, Composition

Origin

Crude petroleum formed from marine organisms buried over millions of years under high pressure; *complex mixture of hydrocarbons (alkanes, cycloalkanes, aromatics) + sulfur/N/O compounds*.

Composition

C	80–90%
H	10–14%
S	0.1–3%
N	0.1–2%
O	up to 2%

Hydrocarbon Types

- Paraffins (alkanes)
- Naphthenes (cycloalkanes)
- Aromatics
- Small amount alkenes/alkynes

Fractional Distillation of Petroleum

Process

Crude petroleum heated to $\sim 400^\circ$C; vapours pass into fractionating column; different fractions condense at different levels based on boiling point.

Fraction	B.P. ($^\circ$C)	Uses
Refinery gas	< 20	LPG, fuel gas
Gasoline/Petrol	20–70	Fuel for cars
Naphtha	70–120	Solvent, chemical feedstock
Kerosene	150–250	Jet fuel, heating
Diesel oil	250–350	Diesel engines
Fuel oil	350–400	Furnaces, ships
Lubricating oil	>400	Lubrication
Bitumen/Asphalt	Residue	Road paving, waterproofing

Cracking of Petroleum

Definition

Cracking: Breaking down of large, heavy hydrocarbon molecules into smaller, more useful ones (especially petrol-range C_5–C_{12}) by heat, pressure, or catalysts.

Thermal Cracking

500–700°C, 10–70 atm
No catalyst
Gives more alkenes
Used for ethylene production

Catalytic Cracking

500°C, lower pressure
Catalyst: zeolite or silica-alumina
Gives more branched alkanes (high octane)
Preferred for petrol production

Example: $C_{16}H_{34} \xrightarrow{\text{cat/heat}} C_8H_{18} + C_8H_{16}$

Knocking and Octane Number

Knocking

Knocking (pinking): Premature auto-ignition of fuel-air mixture in SI engine before spark; causes metallic noise and reduces engine efficiency/life.

Octane Number (ON)

Measure of anti-knock quality of petrol.
ON defined: % iso-octane in a blend of iso-octane (ON=100) and n-heptane (ON=0) that gives same knock as the fuel sample.

Higher ON = less knocking tendency.

Increase ON by: Catalytic cracking | Isomerization | Adding additives (earlier: TEL; now: ethanol, MTBE) | Blending with aromatics

Cetane Number and Diesel Quality

Cetane Number (CN)

Measure of ignition quality of **diesel fuel** in a CI (compression ignition) engine.

CN defined: % cetane (hexadecane, CN=100) in blend with α-methyl naphthalene (CN=0) with same ignition delay as fuel.

Higher CN = **shorter ignition delay** = **better diesel quality**

Feature	Octane vs Cetane
Engine type	SI (spark ignition) vs CI (compression ignition)
Fuel	Petrol / gasoline vs Diesel
High number means	Anti-knock (ON) vs Easy ignition, short delay (CN)
Typical value	Petrol: ON $\approx$ 87–95 vs Diesel: CN $\approx$ 45–55

Gaseous Fuels — Overview

Advantages of Gaseous Fuels

High calorific value per kg	Easy, complete combustion
No ash or smoke	Easy ignition and control
Easily piped/transported	Uniform composition

Fuel	GCV kJ/m^3	Main Components
Natural gas	37000–40000	CH_4 (85%), C_2H_6, CO_2
LPG	93000–97000	Propane (C_3H_8) + Butane (C_4H_{10})
Coal gas	18000–20000	H_2, CH_4, CO
Producer gas	4600–5400	CO, N_2, CO_2, H_2
Water gas	11000–12000	CO (50%), H_2 (45%)
Biogas	21000–25000	CH_4 (60%), CO_2

Natural Gas and LPG

Natural Gas

- Found with petroleum deposits
- **Main:** CH_4 (85–90%)
- Also: C_2H_6, C_3H_8, CO_2, N_2
- GCV $\approx$ 37000 kJ/m^3
- Burns cleanly (CNG for vehicles)
- Transported in pipelines or as LNG

LPG (Liquefied Petroleum Gas)

- Mixture of propane (C_3H_8) and butane (C_4H_{10})
- Stored as liquid under pressure
- Odorant (ethyl mercaptan) added
- GCV $\approx$ 46000 kJ/kg
- **Domestic:** cooking gas
- **Industrial:** heating, autogas

Producer Gas and Water Gas

Producer Gas

Made by: Blowing air through hot coke bed

$2C + O_2 \rightarrow 2CO$
$C + CO_2 \rightarrow 2CO$

Composition: CO 25%, N_2 65%, CO_2 4%, H_2 4%
GCV: $\approx$5000 kJ/m^3 (low)
Uses: Industrial furnaces, not domestic

Water Gas

Made by: Blowing steam through red-hot coke

$C + H_2O \rightarrow CO + H_2$
$CO + H_2O \rightarrow CO_2 + H_2$

Composition: CO 45%, H_2 50%
GCV: $\approx$11600 kJ/m^3
Uses: Fuel, H_2 source

Biogas

What is Biogas?

Gas produced by **anaerobic decomposition** of organic matter (animal dung, agricultural waste, sewage) by methanogenic bacteria.

Composition

CH_4: 55–65%
CO_2: 30–40%
H_2S, N_2, H_2: Small amounts
GCV $\approx$ 22000 kJ/m^3

Advantages

- Renewable; reduces waste
- Low pollution
- Slurry = excellent manure
- Cheap for rural areas
- Reduces deforestation

Combustion of Fuels

Definition

Combustion: Rapid oxidation of a fuel releasing heat and light. Requires fuel, oxygen, and ignition temperature.

Key Combustion Reactions

$C + O_2 \rightarrow CO_2 + 393.5$ kJ
$2H_2 + O_2 \rightarrow 2H_2O + 483$ kJ
$S + O_2 \rightarrow SO_2 + 296$ kJ
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 890$ kJ
$2CO + O_2 \rightarrow 2CO_2 + 566$ kJ

Incomplete combustion: Insufficient $O_2 \Rightarrow$ CO (toxic) formed instead of CO_2. $2C + O_2 \rightarrow 2CO$

Theoretical Air Requirement for Combustion

Formula (Stoichiometric Air)

Minimum air required (by mass) per kg of fuel for complete combustion:

$$\text{Air req.} = \frac{100}{23.2}\,[2.67\,C + 8\,H + S - O] \ \text{ kg air/kg fuel}$$

where C, H, S, O = mass fractions; Air contains 23.2% O_2 by mass.

Derivation Idea

From stoichiometry:
1 kg C needs 8/3 kg O_2; 1 kg H needs 8 kg O_2; 1 kg S needs 1 kg O_2.
Subtract O_2 already in fuel. Divide by 0.232 to get air.

Theoretical Air — Solved Numerical

Problem

Ultimate analysis of fuel: C 85%, H 12%, S 1%, O 2%. Find theoretical air required per kg of fuel.

Solution

O_2 required $= 2.67(0.85) + 8(0.12) + 1(0.01) - 0.02$

$= 2.270 + 0.960 + 0.010 - 0.020 = 3.22$ kg O_2/kg fuel

$$\text{Air required} = \frac{3.22}{0.232} = \textbf{13.88 kg air/kg fuel}$$

Excess air % used in practice = 20–40% above stoichiometric

Flue Gas Analysis — Orsat Apparatus

Principle

Flue gas (combustion products) analyzed volumetrically by absorbing each component:

Step	Absorbent	Gas absorbed	Result
1	KOH solution (33%)	CO_2	% CO_2
2	Pyrogallol + KOH	O_2	% O_2
3	$CuCl/NH_4Cl$ (amm. cuprous chloride)	CO	% CO
4	Remainder	N_2	% N_2 by diff.

Use: Determine combustion efficiency; check for excess air or incomplete combustion

Good combustion: CO_2 high, CO ≈ 0, O_2 low

PYQ — 7-Mark Questions: Unit 4 Fuels

Frequently Asked

1. Explain proximate analysis of coal with procedure and significance. [7]
2. Explain ultimate analysis of coal and its significance. [7]
3. What is Dulong's formula? Calculate GCV and NCV with given analysis. [7]
4. Explain fractional distillation of petroleum with fractions and uses. [7]
5. Explain cracking of petroleum (thermal and catalytic). [7]
6. Explain Orsat apparatus with neat diagram and procedure. [7]
7. Define knocking. Explain octane number and cetane number. [7]
8. Explain LPG and biogas: composition, preparation, uses. [7]

Unit 4 — Numericals Practice Bank

1. Coal: C 70%, H 6%, O 10%, S 2%, Ash 12%. Find GCV and NCV.
2. A fuel has GCV = 50000 kJ/kg, H = 14%. Find NCV.
3. Coal: C 78%, H 5%, O 8%, S 1.5%, N 1%, Ash 6.5%. Find GCV by Dulong's formula.
4. Fuel: C 88%, H 10%, S 0.5%, O 1.5%. Find theoretical air required per kg of fuel.
5. NCV of a fuel = 42000 kJ/kg; H = 11%. Find GCV.
6. Proximate analysis: M=5%, VM=32%, Ash=8%. Find fixed carbon. % and comment on fuel quality.

Unit 4 — Midpoint Summary

Topic	Key Point
Classification	Solid/Liquid/Gas; Natural/Artificial
GCV vs NCV	GCV = water condensed; NCV = water as steam
Dulong's formula	GCV = 33800C + 144000(H-O/8) + 9390S
Coal types	Peat < Lignite < Bituminous < Anthracite (rank order)
Proximate analysis	M, VM, Ash, FC — by heating
Ultimate analysis	C, H, N, S, O, Ash — elemental; used for Dulong
Petroleum fractions	8 fractions from refinery gas to bitumen
Cracking	Thermal: high temp; Catalytic: zeolite (better quality)
Octane/Cetane	ON for petrol (anti-knock); CN for diesel (easy ignition)
Producer gas	Low GCV ($CO + N_2$); Water gas: High GCV ($CO + H_2$)

Reforming of Petroleum

Definition

Reforming: Conversion of low-octane straight-chain hydrocarbons into high-octane branched/aromatic ones *without* changing molecular weight. Uses Pt/Re catalyst at 500°C, 15–35 atm (**catalytic reforming**).

Key Reactions

n-hexane $\rightarrow$ 2-methylpentane	Isomerization
Cyclohexane $\rightarrow$ benzene $+ 3H_2$	Dehydrogenation
n-heptane $\rightarrow$ toluene $+ 4H_2$	Aromatization

Result: High-octane reformate used directly in petrol; H_2 byproduct used in hydrotreating.

Synthetic Petrol — Fischer-Tropsch Process

Fischer-Tropsch Synthesis

Production of liquid hydrocarbons (synthetic petrol) from **syngas** ($CO + H_2$) using Fe or Co catalyst at 150–300°C.

$$n\,CO + (2n+1)\,H_2 \xrightarrow{Fe/Co} C_nH_{2n+2} + n\,H_2O$$

Bergius Process (Hydrogenation of Coal)

$$\text{Coal} + H_2 \xrightarrow{400^\circ C,\ 200\ atm,\ Fe\ catalyst} \text{liquid hydrocarbons (synthetic petrol)}$$

Used in Germany during WWII; important for coal-rich/oil-poor nations.

Gasoline Quality and Anti-Knock Additives

Why Additives?

Straight-run petrol from distillation has ON $\approx$ 60–70. Modern engines require ON $\geq$ 87. Additives/processes raise ON.

Additive/Process	Note
TEL (tetraethyl lead)	Historically used; banned now (toxic Pb pollution)
MTBE	Methyl tert-butyl ether; oxygenate; phased out in USA
Ethanol blending	E10, E20 blends; renewable; common today
Aromatics addition	Benzene, toluene raise ON; limited for health reasons
Catalytic reforming	Best industrial method; produces high-ON reformate
Isomerization	n-butane $\rightarrow$ isobutane; $\uparrow$ON without aromatics

Fuel Combustion and Air Pollution

Major Pollutants from Fuel Combustion

Pollutant	Source	Effect
CO	Incomplete combustion	Haemoglobin binds; asphyxiation
CO_2	All combustion	Greenhouse gas, climate change
SO_2	S in coal/oil	Acid rain, respiratory problems
NO_x	High-temp combustion	Smog, acid rain
Particulates	Coal, heavy oil	Lung damage
HC vapours	Engine blowby	Smog precursor (photochemical)

Mitigation: Catalytic converters | Flue gas desulfurization | LNG/CNG use | EGR (exhaust gas recirculation) | High-efficiency combustion

Calorific Value of Gaseous Fuels — Calculation

Method for Gaseous Fuels

GCV of a gaseous fuel mixture $= \sum$ (mole fraction $\times$ GCV of component)

Alternatively, use combustion enthalpy of each component from standard values.

Solved Example

Coal gas composition (by volume): H_2 52%, CH_4 33%, CO 8%, CO_2 3%, N_2 4%

GCV of $H_2 = 12770$, $CH_4 = 35880$, CO $= 12630$ kJ/m^3

$$\text{GCV} = 0.52 \times 12770 + 0.33 \times 35880 + 0.08 \times 12630 + 0 + 0$$
$$= 6640 + 11840 + 1010 = \mathbf{19490\ kJ/m^3}$$

Excess Air and Combustion Efficiency

Why Use Excess Air?

Theoretical air is minimum; in practice **20–50% excess air** is supplied to ensure complete combustion and avoid CO formation.

Too Little Air

Incomplete combustion
CO formed (toxic)
Soot/smoke produced
Low heat release
Fuel wastage

Too Much Excess Air

Excess N_2 heated unnecessarily
Heat carried away in flue gas
Lower thermal efficiency
Excessive NO_x at high temp

Optimum: Orsat analysis guides control — aim for CO_2 max, CO ≈ 0.

Renewable and Alternative Fuels

Fuel	Source/Production	Advantages
Biogas	Anaerobic digestion	Renewable; waste utilization
Ethanol	Fermentation of sugars	Blended with petrol; lower CO
Biodiesel	Transesterification of oils	Blended with diesel; biodegradable
Hydrogen	Electrolysis / steam reforming	Zero CO_2 at point of use
Syngas	Coal/biomass gasification	Flexible feedstock
Methanol	$CO + 2H_2$ (from biomass)	Liquid; high ON (115)

India: National Biofuel Policy mandates 20% ethanol blending (E20) by 2025; PM-JIVANyojana for 2G ethanol from bagasse.

Numerical — Flue Gas Analysis

Problem

Flue gas analysis by Orsat: $CO_2 = 12\%$, $O_2 = 6\%$, $CO = 2\%$, $N_2 = 80\%$. Fuel: C 85%, H 10%, S 0%, O 5%. Find theoretical air per kg fuel and % excess air.

Solution

Theoretical $O_2 = 2.67(0.85) + 8(0.10) - 0.05 = 2.27 + 0.80 - 0.05 = 3.02$ kg

Theoretical air $= 3.02/0.232 = 13.02$ kg

$$\text{Excess air } \% = \frac{\%O_2 - \frac{1}{2}\%CO}{\%N_2} \times \frac{N_2 \text{ (of air)}}{O_2 \text{ (of air)}} \times 100$$

Simplified: $\approx \frac{6-1}{80} \times \frac{79}{21} \times 100 \approx \mathbf{23.6}\%$

Coal Tar — Fractions and Uses

What is Coal Tar?

Black, viscous liquid byproduct of HTC of coal. Contains >300 organic compounds (benzene, toluene, naphthalene, anthracene, phenol, etc.).

Fraction	B.P. (°C)	Products/Uses
Light oil	<170	Benzene, toluene, xylene (solvents)
Middle oil	170–230	Phenol, cresol (disinfectants), naphthalene
Heavy oil	230–270	Naphthalene (mothballs), basic dyes
Anthracene oil	270–360	Anthracene (dyes), phenanthrene
Pitch	>360	Road making, waterproofing, electrodes

Comparison of Industrial Gaseous Fuels

Feature	Coal Gas	Producer	Water Gas	Natural Gas
Source	HTC coal	Air + coke	Steam + coke	Underground
CH_4 %	28–35	<1	0	85
H_2 %	50	4	48	Trace
CO %	8	25	45	0
N_2 %	4	65	5	3
GCV kJ/m^3	18000	5000	11600	37000
Toxicity	Toxic (CO)	Very toxic	Toxic	Non-toxic

Bomb Calorimeter — GCV Measurement

Principle

Known mass of fuel burned with excess O_2 in sealed steel bomb immersed in a calorimeter. Heat released raises temperature of known mass of water.

$q = (m_w c_w + W) \times \Delta T$

where W = water equivalent of calorimeter, $m_w c_w$ = heat capacity of water.

$\text{GCV} = q / m_{\text{fuel}}$

Note: Bomb calorimeter gives **GCV** (water condensed at high pressure). Bomb calorimeter cannot give NCV directly.

Comparison of Solid, Liquid and Gaseous Fuels

Property	Solid	Liquid	Gaseous
GCV (kJ/kg)	15000–36000	42000–50000	High per kg
Handling	Difficult	Easy	Easiest (pipeline)
Storage	Easy, cheap	Easy (tanks)	Difficult (pressure)
Ignition	High temp	Easy	Easiest
Combustion control	Poor	Good	Best
Ash produced	Yes	No	No
Pollution	Most	Moderate	Least
Transport	Rail/road	Tanker/pipeline	Pipeline/cylinder

PYQ Short-Answer Practice (2-mark)

1. Define GCV and NCV. How are they related?
2. What is Dulong's formula? Name all terms.
3. Differentiate thermal and catalytic cracking.
4. Define octane number and cetane number.
5. What is knocking? How can it be reduced?
6. List four fractions of petroleum with their uses.
7. What is proximate analysis? Which heating steps are used?
8. What is producer gas? Give composition.
9. What is water gas? How is it prepared?
10. Define bomb calorimeter. What does it measure?
11. Why is excess air used in combustion?
12. Name the absorbents used in Orsat apparatus.

Exam Tips — Unit 4: Fuels

Do's

- Show full substitution in Dulong's formula
- Write combustion reactions for each element separately
- For proximate: state temperature and time at each step
- Remember: FC $= 100 - (\text{M} + \text{VM} + \text{Ash})$
- For Orsat: state absorbents in correct order (CO_2 first)

Don'ts

- Don't confuse GCV and NCV (GCV $>$ NCV always)
- Don't forget to subtract O/8 in Dulong's formula
- Don't swap octane (petrol) and cetane (diesel)
- Don't forget to use mass fractions (not percent) in formulas
- Don't use 21% O_2 in mass-basis air calc — use 23.2%

Unit 4 — Revision Flash Points

Key Fact	Value / Rule
GCV kJ/kg (wood)	$\approx$17000
GCV kJ/kg (coal)	25000–36000
GCV kJ/kg (petrol)	$\approx$47000
GCV kJ/kg (diesel)	$\approx$45000
Latent heat (steam)	2442 kJ/kg (used in NCV calc)
Air = 23.2% O_2	Mass basis for air calc
Orsat order	$CO_2 \rightarrow O_2 \rightarrow CO \rightarrow N_2$
Proximate: FC	FC = 100 − M − VM − Ash
Dulong formula	33800C + 144000(H−O/8) + 9390S
Cracking catalyst	Zeolite / silica-alumina (FCC)

Numerical Variations — GCV and NCV

Type 1: Find NCV from GCV

Fuel: GCV $= 35000$ kJ/kg, H $= 4\%$
NCV $=$ GCV $- 9H \times 2442 = 35000 - 9(0.04)(2442)$
$= 35000 - 879.1 =$ **34120.9 kJ/kg**

Type 2: Find GCV from NCV

Fuel: NCV $= 42700$ kJ/kg, H $= 13\%$
GCV $=$ NCV $+ 9H \times 2442 = 42700 + 9(0.13)(2442)$
$= 42700 + 2857.1 =$ **45557.1 kJ/kg**

Tip: GCV is always greater than NCV for fuels containing hydrogen.

Proximate Analysis — Numerical

Problem

A coal sample gave: Initial mass = 2 g
After drying at 110°C: 1.92 g
After heating at 950°C (closed): 1.32 g
After heating at 700°C (open): 0.28 g
Find: M%, VM%, Ash%, FC%

Solution

$$\text{Moisture} = \frac{2 - 1.92}{2} \times 100 = \mathbf{4\%}$$

$$\text{VM} = \frac{1.92 - 1.32}{2} \times 100 = \mathbf{30\%}$$

$$\text{Ash} = \frac{0.28}{2} \times 100 = \mathbf{14\%}$$

$$\text{FC} = 100 - 4 - 30 - 14 = \mathbf{52\%}$$

Ultimate Analysis — Numerical (Dulong)

Problem

Ultimate analysis: C = 80%, H = 8%, S = 2%, N = 2%, O = 6%, Ash = 2%.
Find GCV and NCV.

Solution

$$\text{GCV} = 33800(0.80) + 144000\left(0.08 - \frac{0.06}{8}\right) + 9390(0.02)$$
$$= 27040 + 144000(0.08 - 0.0075) + 187.8$$
$$= 27040 + 144000(0.0725) + 187.8$$
$$= 27040 + 10440 + 187.8 = \mathbf{37668\ kJ/kg}$$
$$\text{NCV} = 37668 - 9(0.08)(2442) = 37668 - 1758 = \mathbf{35910\ kJ/kg}$$

Numerical — Theoretical Air (GTU Style)

Problem

Coal: C 75%, H 5%, S 2%, O 10%, N 5%, Ash 3%.
Find (a) theoretical air per kg fuel, (b) volume of air at STP per kg fuel.

Solution

O_2 needed $= 2.67(0.75) + 8(0.05) + 0.02 - 0.10$
$= 2.003 + 0.40 + 0.02 - 0.10 = 2.323$ kg O_2

(a) Air $= 2.323/0.232 =$ **10.01 kg/kg fuel**

(b) Volume at STP: mol $O_2 = 2.323/32 = 0.0726$ kmol
Air $= 0.0726/0.21 = 0.346$ kmol $= 0.346 \times 22.4 =$ **7.74 m^3/kg fuel**

Unit 4 — PYQ Pattern Analysis

Topic	May 23	Nov 23	May 24
Proximate analysis	7	–	7
Ultimate analysis + Dulong	7	7	–
GCV/NCV numerical	3	3	3
Cracking	–	7	7
Petroleum fractions	3	–	3
Gaseous fuels (LPG/Biogas)	–	3	–
Orsat apparatus	7	–	7
Octane/Cetane number	3	3	3
Air for combustion	3	3	–
Coal types	–	3	–

Most likely 7-mark: Proximate analysis **OR** Dulong numerical **OR** Orsat apparatus

Combustion Numericals — More Practice

1. Fuel: C 72%, H 4%, O 8%, S 1%, Ash 15%. Find GCV by Dulong's.
2. GCV = 40000 kJ/kg, H = 16%. Find NCV.
3. Fuel: C 88%, H 9%, O 2%, S 1%. Find theoretical O_2 and air per kg.
4. If 30% excess air is used, find actual air per kg for above fuel.
5. Bomb calorimeter: m = 0.9 g fuel, $\Delta T = 2.5^\circ$C, water = 2000 g, W = 500 g. Find GCV.
6. Gaseous fuel: H_2 40%, CO 50%, N_2 10% (by vol). Find GCV (kJ/m^3).

Petroleum Refining — Complete Picture

Refinery Operations Summary

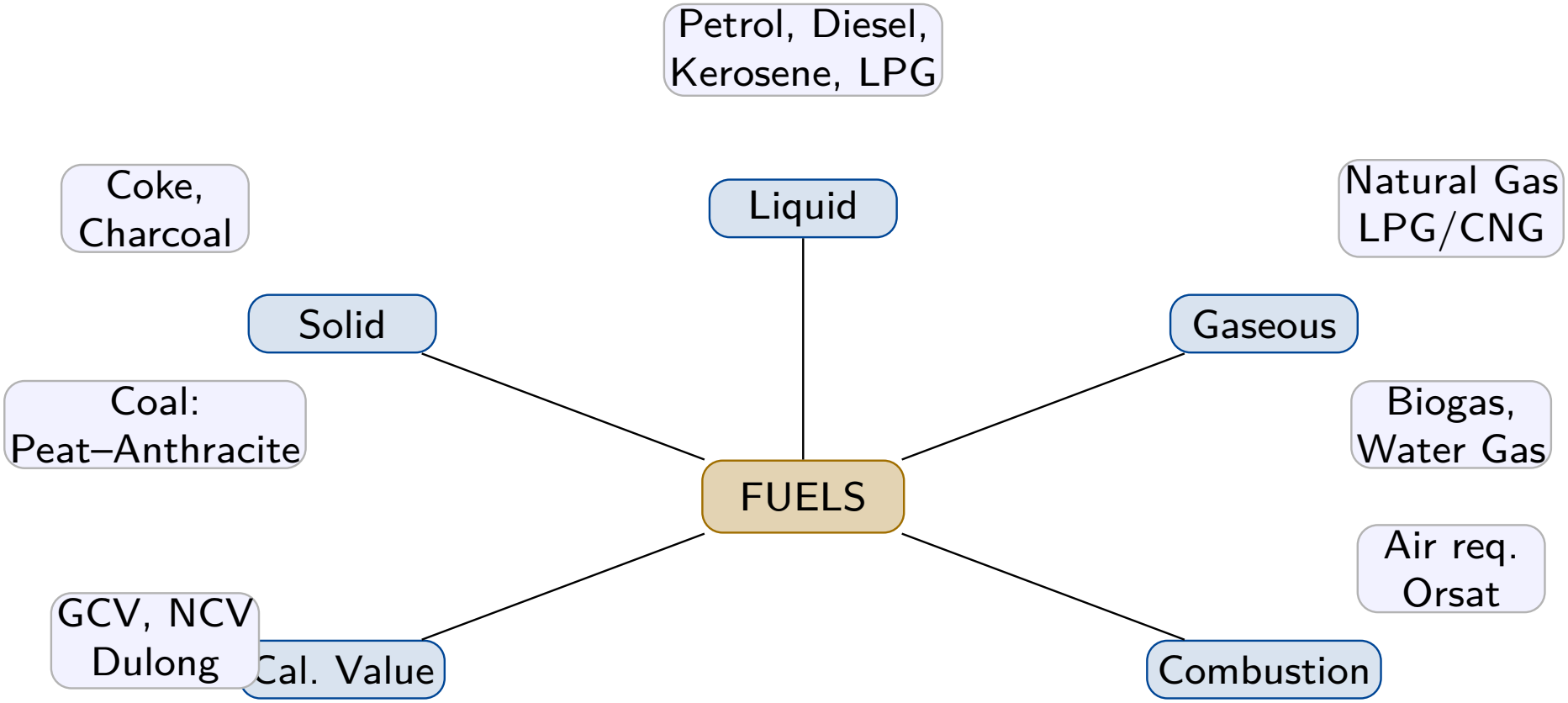
Process	Input → Output
Atmospheric distillation	Crude oil → LPG, petrol, kerosene, diesel, fuel oil
Vacuum distillation	Residue → lube oil, wax, bitumen
Thermal cracking	Heavy gas oil → alkenes (ethylene)
Catalytic cracking (FCC)	Heavy distillate → high-octane gasoline
Catalytic reforming	Naphtha → high-octane reformate + H_2
Hydrotreating	All fractions → desulfurized products
Isomerization	n-butane/pentane → high-octane isoalkanes

Flash Point, Fire Point and Self-Ignition Temperature

Property	Definition	Significance
Flash point	Lowest temp at which vapours momentarily ignite when flame is applied	Fire safety; storage classification
Fire point	Temp at which vapours sustain combustion for $\geq$5 s	More conservative safety limit
Self-ignition temp (SIT)	Temp at which fuel ignites without external flame	Engine knock; spontaneous fire risk

Typical values: Petrol FP $= -43^{\circ}$C (very flammable) | Diesel FP $= 52^{\circ}$C | Kerosene FP $= 38^{\circ}$C
Higher flash point = safer storage.

Unit 4 — Fuels Mind Map



Unit 4 — Key Formulas Summary

Formula	Variables
$\text{GCV} = 33800C + 144000(H - O/8) + 9390S$	C,H,O,S = mass fractions
$\text{NCV} = \text{GCV} - 9H \times 2442$	H = mass fraction
$\text{Air} = \dfrac{2.67C + 8H + S - O}{0.232}$	per kg fuel (mass basis)
$FC = 100 - M - VM - \text{Ash}$	All in %
$q = (m_w c_w + W)\Delta T$	Bomb calorimeter
$\text{GCV (gas)} = \sum x_i \cdot \text{GCV}_i$	x_i=vol. fraction

Coal vs Petroleum — Comparison

Feature	Coal	Petroleum
State	Solid	Liquid
Origin	Plant matter	Marine organisms
Main element	C (50–95%)	C+H (alkanes, cycloalkanes)
GCV (kJ/kg)	15000–36000	40000–50000
Sulfur content	0.5–3%	0.1–3%
Handling	Difficult	Easy
Combustion control	Poor	Good
Ash produced	Yes	No
Products of processing	Coke, tar, gas	Petrol, diesel, kerosene, LPG
Reserves (India)	Large	Limited

Environmental Impact of Fossil Fuels

Greenhouse Effect

Combustion of fossil fuels releases CO_2 (main GHG), CH_4 (natural gas leaks), and N_2O. These trap heat in the atmosphere, raising global temperatures (**global warming**).

Other Environmental Effects

Acid rain	SO_2 + NO_x from coal/oil power plants
Photochemical smog	NO_x + VOC + sunlight (ozone, PAN)
Particulate pollution	Coal combustion, diesel engines
Oil spills	Tanker accidents; marine ecosystem damage

Hydrogen — The Future Fuel

Why Hydrogen?

High GCV	$\approx$143000 kJ/kg (highest of all fuels)
Zero CO_2 at use	$2H_2 + O_2 \rightarrow 2H_2O$ only
Renewable (if green)	Electrolysis using solar/wind power
Versatile	Fuel cells, IC engines, heating

Challenges

Storage (very low density gas; cryogenic or high-pressure tanks) | Production cost (green H_2 still expensive) | Safety (highly flammable, widest flammability range: 4–75% in air)

Unit 4 — Complete Summary Table

Topic	Core Outcome
Classification	Solid/liquid/gas; natural/artificial
GCV vs NCV	GCV $>$ NCV; diff $=$ latent heat of steam
Dulong's formula	GCV from elemental analysis (C, H, O, S)
Proximate analysis	M, VM, Ash, FC by stepwise heating
Ultimate analysis	Elemental %; used for Dulong
Petroleum fractions	8 fractions; fractional distillation
Cracking	Thermal (alkenes) vs Catalytic (high-ON petrol)
Octane/Cetane	ON for petrol; CN for diesel
Gaseous fuels	Natural gas (CH_4), LPG, biogas, producer/water gas
Orsat apparatus	$CO_2 \rightarrow O_2 \rightarrow CO \rightarrow N_2$; checks combustion efficiency

Unit 4 Complete — Bridge to Unit 5: Lubricants

Unit 4 in One Line

Fuels are substances that release heat on combustion; coal and petroleum are primary fossil fuels obtained by geological processes; their quality is measured by calorific value (Dulong's formula for solid/liquid, stoichiometry for gases); combustion efficiency is monitored by Orsat analysis.

Coming Next — Unit 5: Lubricants

Unit 5 covers **classification of lubricants** (liquid, semi-solid, solid), mechanisms of lubrication, essential properties (viscosity, flash/fire point, cloud/pour point, acid value, saponification number, aniline point), and their applications.

Unit 5: Lubricants

Engineering Chemistry — DI01000071

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April 2, 2026

Unit 5 covers classification of lubricants, mechanisms of lubrication, essential properties (viscosity, flash/fire point, cloud/pour point, acid value, saponification number, aniline point), and industrial applications.

Unit 5 — Topics and Weightage

Topics at a Glance

#	Topic	Key Concepts
1	Definition and functions	Reduce friction, wear, heat
2	Classification	Liquid, semi-solid, solid
3	Liquid lubricants	Mineral, vegetable, animal, blended
4	Greases	Semi-solid; extreme pressure
5	Solid lubricants	Graphite, MoS_2; high-temp use
6	Mechanisms	Hydrodynamic, boundary, extreme pressure
7	Viscosity and index	Resistance to flow; VI improvers
8	Flash/fire point	Safety; volatile impurities
9	Cloud/pour point	Low-temp performance
10	Acid value, saponification	Quality, degradation
11	Aniline point	Aromatic content indicator

Weightage: $\approx$10% | GTU: 2 $\times$ 7-mark + short answers

Lubricants — Definition and Functions

Definition

A **lubricant** is any substance introduced between two moving surfaces to reduce **friction**, **wear**, and **heat generation**.

Functions of a Lubricant

1. Reduce friction between moving parts
2. Minimize wear and surface damage
3. Carry away heat generated at contact surfaces
4. Prevent corrosion/rust on metal surfaces
5. Act as a seal (prevent entry of dust, moisture)
6. Absorb shocks between machine parts
7. Carry away metal particles and contaminants

Classification of Lubricants

Type	Subtype	Examples
Liquid	Mineral oils	Engine oil, turbine oil, hydraulic oil
	Vegetable oils	Castor oil, olive oil, palm oil
	Animal oils	Lard oil, fish oil, sperm oil
Semi-solid	Greases	Calcium, lithium, sodium grease
Solid	Organic	Graphite, MoS_2, PTFE (Teflon)
	Inorganic	Talc, mica, silica powder

Selection basis: Load, speed, temperature, environment, compatibility with materials.

Liquid Lubricants — Mineral Oils

Mineral Oils

Derived from petroleum refining (lube oil fraction, B.P. $>400^{\circ}$C). Most widely used lubricants. Contain paraffinic, naphthenic, and aromatic hydrocarbons.

Paraffinic Oils

High viscosity index (VI)
Good oxidation resistance
High pour point (wax content)
Best for engine oils

Naphthenic Oils

Low pour point (less wax)
Lower VI than paraffinic
Good for low-temperature use
Used in refrigeration systems

Greases — Semi-Solid Lubricants

What is Grease?

Grease = Mineral oil + thickener (metallic soap) + additives.
Semi-solid consistency; stays in place without leaking; used where liquid oil cannot be retained.

Type	Thickener	Properties / Uses
Calcium grease	Ca soap	Water resistant; chassis, bearings
Sodium grease	Na soap	Not water resistant; high temp. use
Lithium grease	Li soap	Multi-purpose; water resistant; best overall
Barium grease	Ba soap	EP (extreme pressure) use
Bentonite grease	Clay	No drop point; high-temp

Solid Lubricants

When Are Solid Lubricants Used?

At very high temperatures or high pressures where oils/greases fail; in vacuum (space); where contamination by oil is not permitted (food, textile).

Graphite

Layered hexagonal structure; weak van der Waals forces between layers allow easy shear
Good up to $\sim$500°C in air
Needs adsorbed vapour (poor in vacuum!)
Burns above 650°C

MoS_2 (Molybdenum Disulfide)

Layered hexagonal structure; low friction in vacuum (unlike graphite)
Good up to $\sim$350°C
Excellent for aerospace, high-vacuum applications

Mechanisms of Lubrication

Mechanism	Film Condition	Characteristics
Hydrodynamic (fluid film)	Thick film; surfaces fully separated	Lowest friction; no metal contact; ideal
Elasto-hydrodynamic (EHD)	High-pressure thin film	Gears, rolling bearings; film forms under load
Boundary lubrication	Very thin film; surfaces nearly contact	High load, low speed; additive chemistry critical
Extreme pressure (EP)	Metal-to-metal contact	EP additives (S, P, Cl compounds) react with metal to form low-shear films

Stribeck curve: Shows transition from boundary $\rightarrow$ mixed $\rightarrow$ hydrodynamic as speed$\times$viscosity/load increases.

Viscosity — Definition and Significance

Definition

Viscosity = resistance of a fluid to flow. It is the **most important** property of a lubricant.

Dynamic viscosity (η): $\tau = \eta \cdot \dfrac{dv}{dy}$ (Pa·s or poise)

Kinematic viscosity (ν): $\nu = \eta/\rho$ (m^2/s or cSt)

Too low viscosity	Insufficient film; metal contact; wear
Too high viscosity	High internal friction; power loss; poor circulation
Ideal	Lowest viscosity that still maintains full lubrication film

Viscosity Index (VI)

Definition

Viscosity Index (VI): An empirical number indicating how much the viscosity of an oil changes with temperature.

High VI = viscosity changes *less* with temperature = better oil for wide temperature range

VI Scale (Dean and Davis)

Reference oils: Pennsylvania oil (paraffinic) = VI 100 | Gulf Coast oil (naphthenic) = VI 0

$$\text{VI} = \frac{L - U}{L - H} \times 100$$

where L = viscosity of VI-0 oil, H = viscosity of VI-100 oil, U = viscosity of test oil (all at 40°C, referenced to 100°C viscosity)

Flash Point and Fire Point

Flash Point

Lowest temperature at which lubricant vapour **momentarily ignites** when a flame is applied (vapours flash but don't sustain burning).

Significance:
– Safe operating temperature
– Detect volatile impurities
– Higher FP = safer use

Fire Point

Temperature at which vapours **sustain continuous burning** for at least 5 seconds.

Fire point > Flash point (always)

Typical:
Engine oil FP $\approx 200^\circ$C
Fire point $\approx 220^\circ$C

Test methods: Pensky-Martens (closed cup) and Cleveland (open cup) apparatus.

Cloud Point and Pour Point

Cloud Point

Temperature at which a lubricating oil first becomes **cloudy or hazy** when cooled, due to precipitation of wax crystals.

Significance: Indicates start of wax separation; wax may clog filters/pipes

Pour Point

Lowest temperature at which an oil **still flows** (can be poured) when cooled under standard conditions.

Pour point = last temperature at which flow observed + 3°C

Pour point > **Cloud point** always

Low pour point required for lubricants used in cold climates (arctic gear oils), refrigeration, aviation.

Acid Value (Acid Number)

Definition

Acid value (AV): Number of milligrams of KOH required to neutralize the free acids present in **1 gram** of lubricating oil.

Units: mg KOH / g oil

Significance

Fresh oil	Low AV (few free acids)
Degraded/oxidized oil	High AV (acids formed by oxidation, hydrolysis)
High AV	Corrosive to metals; oil must be changed

AV is a measure of oil deterioration in service.

Saponification Number (Value)

Definition

Saponification number (SN): Number of milligrams of KOH required to saponify (hydrolyze) the esters present in **1 gram** of oil.

Units: mg KOH / g oil

Significance

Mineral oil	Low SN ($\approx$0; no esters)
Vegetable oil	High SN (many ester linkages)
Animal fat	High SN
Blended oil	Intermediate SN

SN indicates the proportion of fatty oils (esters) in the lubricant.

Aniline Point

Definition

Aniline point: Lowest temperature at which equal volumes of aniline and lubricating oil are **completely miscible** (form a single phase).

Units: $^{\circ}$C

Significance

Low aniline point	High aromatic content (dissolves aniline easily)
High aniline point	High paraffinic content (less aromatic)

Low aniline point: Oil will swell rubber seals/gaskets (not suitable where rubber is present)
High aniline point: Safe for rubber seals; paraffinic oil

Oiliness (Lubricity)

Definition

Oiliness (lubricity): The ability of a lubricant to **adhere to metal surfaces** and form a thin, tenacious boundary film even under high load and low speed (boundary lubrication regime).

High oiliness	Fatty acids, esters, animal oils
Low oiliness	Pure mineral oils
Improvement	Add oiliness agents (fatty acids, sulfur compounds, EP additives)

Oiliness **cannot** be measured by viscosity — it depends on film-forming ability and molecular polarity.

Emulsification and Demulsibility

Emulsification

Formation of a stable oil-water mixture (emulsion).

Desirable when: Cutting fluids, soluble oils (cooling + lubrication in machining).

Emulsifying agents (soaps) stabilize the emulsion.

Demulsibility

Ability of oil to **separate from water** quickly after mixing (high demulsibility = good).

Desirable when: Turbine oils, hydraulic oils — water contamination should be removed quickly.

High water retention $\Rightarrow$ corrosion, foaming, poor lubrication.

Lubricant Additives

Additive	Example	Function
Antioxidants	Phenols, ZnDTP	Prevent oil oxidation and gum formation
Antiwear (AW)	ZnDTP	Reduce wear under moderate loads
Extreme pressure (EP)	S, P, Cl compounds	Form low-shear films under very high load
Viscosity index improvers	Polymethacrylates	Reduce viscosity-temperature sensitivity
Pour point depressants	Alkyl naphthalenes	Prevent wax crystal growth at low temp
Detergents/dispersan	Sulfonates, PIBSA	Keep engine clean; disperse soot/sludge
Corrosion inhibitors	Benzotriazole	Protect metal surfaces
Antifoam agents	Silicones	Prevent foam formation

Refining of Mineral Lubricating Oils

Steps in Lube Oil Refining

Lube oil fraction from vacuum distillation is further refined to remove unwanted components:

#	Process	Purpose
1	Deasphalting	Remove asphaltenes (propane extraction)
2	Solvent extraction	Remove aromatics; improve VI (NMP or furfural)
3	Dewaxing	Remove wax; lower pour point (MEK-toluene)
4	Hydrotreating	Remove S, N; oxidation stability; brighten colour
5	Blending	Add base oil + additives for final grade

SAE Viscosity Grades for Engine Oils

SAE Classification

SAE (Society of Automotive Engineers) grades classify oils by viscosity.
W grades (e.g. 0W, 5W, 10W): Low-temperature cranking viscosity (winter)
Summer grades (e.g. 20, 30, 40, 50): High-temperature viscosity

Multigrade Oils

5W-30, 10W-40, 15W-50: Multigrade oils satisfy *both* cold-start (W grade) and hot-running (summer grade) requirements.

Achieved by adding viscosity index improver polymers to a lower-grade base oil.

Vegetable and Animal Oils as Lubricants

Vegetable Oils

Castor oil	High viscosity; good boundary
Olive oil	Food-grade equip.
Palm oil	Textile machines

Pros: Renewable; biodegradable; good oiliness

Cons: Oxidize easily; gum formation; poor at high temp

Animal Oils

Lard oil	Watch, clocks
Sperm oil	Clocks, instruments
Fish oil	leather processing

Pros: Excellent boundary lubrication; natural EP

Cons: Oxidize fast; rancidity; limited temp range

Synthetic Lubricants

Why Synthetic Lubricants?

Designed molecules with precisely tailored properties; outperform mineral oils at extremes of temperature and load.

Type	Example	Application
Poly-α-olefins (PAO)	Mobil 1	Automotive engines; wide temp range
Polyol esters	Pentaerythritol ester	Jet engines, compressors
Phosphate esters	Skydrol	Fire-resistant hydraulic fluids
Silicones	PDMS	High-temp greases; inert with plastics
Polyglycols (PAG)	PEG-based	Compressors, gear boxes
Perfluoropolyethers	Fomblin	Vacuum pumps, space

Cutting Fluids (Metalworking Lubricants)

Purpose of Cutting Fluids

During machining operations (turning, drilling, milling): reduce friction at tool-workpiece interface, cool the cutting zone, and flush away chips.

Type	Composition	Best For
Straight oils	Mineral + EP additives	Heavy-duty; gear cutting, broaching
Soluble oils	Oil-in-water emulsion	General turning, grinding; good cooling
Semi-synthetic	Oil + water + additives	Versatile; low residue
Synthetic	Water + chemicals (no oil)	Grinding; maximum cooling

Key rule: High speed $\Rightarrow$ prioritize cooling (water-based). High load $\Rightarrow$ prioritize lubrication (oil-based).

Properties of Lubricants — Summary Table

Property	Test Method	What It Tells
Viscosity	Ostwald/Redwood	Flow resistance; film thickness
Viscosity Index	ASTM D2270	Temp sensitivity of viscosity
Flash point	Pensky-Martens	Max safe operating temp; impurities
Fire point	Cleveland open cup	Sustained ignition temp
Cloud point	ASTM D2500	Wax separation temperature
Pour point	ASTM D97	Low-temp flow limit
Acid value	Titration with KOH	Free acid content; oil degradation
Saponification no.	Reflux with KOH	Ester (fatty oil) content
Aniline point	ASTM D611	Aromatic content; rubber compatibility
Oiliness	Pin-on-disc friction	Boundary film formation ability

PYQ — 7-Mark Questions: Unit 5 Lubricants

Frequently Asked

1. Define lubricant. Explain its functions and classification. [7]
2. Explain viscosity and viscosity index with significance. [7]
3. Define flash point, fire point, cloud point, pour point with significance. [7]
4. Explain acid value and saponification number as properties of lubricants. [7]
5. Distinguish mineral oil, vegetable oil, and synthetic lubricants. [7]
6. Explain greases: composition, types, and uses. [7]
7. What are solid lubricants? Compare graphite and MoS_2. [7]
8. Explain the mechanisms of lubrication (hydrodynamic, boundary, EP). [7]

Unit 5 — Midpoint Summary

Topic	Key Point
Definition	Reduce friction, wear, heat; protect surfaces
Classification	Liquid, semi-solid (grease), solid
Mineral oil	Petroleum fraction; paraffinic or naphthenic
Grease	Oil + metallic soap; Li grease is multipurpose
Solid lubricants	Graphite (needs moisture); MoS_2 (works in vacuum)
Viscosity	Most important property; measured in cSt
Viscosity Index	High VI = less change with temperature
Flash/Fire point	Safety; detect volatile impurities
Cloud/Pour point	Low-temperature performance
Acid value	mg KOH/g; indicates oil degradation
Saponification no.	mg KOH/g; indicates ester (fatty oil) content
Aniline point	Low AP = aromatic oil; swells rubber seals

Hydrodynamic Lubrication — Mechanism

Principle

At sufficiently high speed, a converging oil wedge builds up pressure between moving surfaces, completely **separating them with a fluid film**. No metal-to-metal contact occurs.

Conditions Required

Sufficient speed	Maintains the oil wedge pressure
Adequate viscosity	Too thin = film breaks; too thick = losses
Converging geometry	Oil dragged into the contact zone
Continuous oil supply	Must not starve

Examples: Journal bearings (crankshaft main bearings), thrust bearings, oil-film slider pads

Extreme Pressure (EP) Lubrication

When is EP Lubrication Needed?

Under very high contact pressures and shock loads (hypoid gear sets, heavily loaded cams) the oil film is squeezed out. EP additives are needed to prevent seizure.

How EP Additives Work

EP additives (S, P, Cl, or Zn compounds) react chemically with metal surface at the high interface temperature ($\sim$200–700°C) to form a sacrificial **iron sulfide / iron phosphide / iron chloride** layer.

This layer has **low shear strength** and prevents metal welding (scuffing/seizure).

Degradation of Lubricants in Service

Cause	Effect	Indicator
Oxidation	Acids, gum, varnish	High acid value; colour change
Thermal decomposition	Cracking; sludge	Viscosity change; dark colour
Water contamination	Emulsion; corrosion	Milky appearance; rust
Metal particles	Catalyse oxidation	Spectrometric analysis
Additive depletion	Loss of protection	High wear metals; AW depleted
Fuel dilution	$\downarrow$ viscosity	Flash point drops

Oil analysis (condition monitoring): Acid value, viscosity, particle count, spectroscopy — used to decide oil change interval.

Comparison of Lubricant Types

Feature	Mineral Oil	Vegetable Oil	Synthetic Oil
Source	Petroleum	Plants	Chemical synthesis
Oxidation stability	Good	Poor	Excellent
Temp range	-30 to 150°C	Limited	-60 to 300°C
VI	80–100	150–200	Up to 200+
Biodegradable	Moderate	Yes	Varies
Cost	Low	Low	High
Oiliness	Moderate	Excellent	Good
Main use	General engineering	Food, environment	Aerospace, extreme conditions

PYQ Short-Answer Practice (2-mark)

1. Define lubricant and state two functions.
2. What is viscosity index? Why is high VI important?
3. Define flash point and fire point. Which is higher?
4. Define cloud point and pour point.
5. What is acid value? Give its significance.
6. What is saponification number?
7. Define aniline point. What does low AP indicate?
8. What is oiliness? How does it differ from viscosity?
9. Compare graphite and MoS_2 as solid lubricants.
10. What is grease? Name its three main components.
11. What are EP additives? Give two examples.
12. Define boundary lubrication.

Numerical — Viscosity Index Calculation

Formula Recap

$$\text{VI} = \frac{L - U}{L - H} \times 100$$

L = kinematic viscosity of VI-0 reference oil at 40°C
H = kinematic viscosity of VI-100 reference oil at 40°C
U = kinematic viscosity of test oil at 40°C (same 100°C viscosity as reference oils)

Solved Example

Test oil at 40°C: U = 75 cSt; L = 120 cSt; H = 50 cSt

$$\text{VI} = \frac{120 - 75}{120 - 50} \times 100 = \frac{45}{70} \times 100 = \mathbf{64.3}$$

Stribeck Curve — Lubrication Regimes

The Stribeck Curve

A plot of **friction coefficient vs.** the Stribeck parameter $\eta N/P$ (viscosity $\times$ speed / load).

Region	Regime	Friction / Film
Low $\eta N/P$	Boundary	High friction; thin adsorbed film; wear
Intermediate	Mixed	Partial film; transition zone; decreasing friction
High $\eta N/P$	Hydrodynamic	Low friction; full fluid film; no wear

Minimum friction is in the hydrodynamic regime. Increase viscosity or speed to move from boundary toward hydrodynamic.

Grease Manufacturing

Process Overview

Grease = **base oil** (70–95%) + **thickener** (3–20%; metallic soap, clay, polyurea) + **additives**.

Metallic soap prepared by saponification: fatty acid + metal hydroxide $\rightarrow$ metal soap + water.

Example: $C_{17}H_{35}COOH + LiOH \rightarrow C_{17}H_{35}COOLi + H_2O$ (lithium stearate)

Drop Point

Drop point: Temperature at which grease loses its semi-solid structure and drips.
Calcium grease: $\approx 80^\circ C$ | Sodium: $\approx 175^\circ C$ | Lithium: $\approx 190^\circ C$ | Bentonite: no drop point

Condition Monitoring of Lubricants

Why Monitor Lubricant Condition?

Regular oil analysis predicts machinery failure, optimizes oil-change intervals, and prevents costly breakdowns (predictive maintenance).

Test	Parameter	Indicates
Viscosity	cSt at 40°C	Dilution (fuel) or oxidation
Acid number (TAN)	mg KOH/g	Oxidation, acid buildup
Base number (TBN)	mg KOH/g	Remaining alkaline reserve
Particle count	ISO cleanliness	Wear, contamination
Elemental analysis	Fe, Cu, Al ppm	Wear of specific components
Karl Fischer water	ppm water	Water contamination

Bio-Lubricants and Green Lubrication

What are Bio-Lubricants?

Lubricants derived from **renewable biological sources** (vegetable oils, animal fats, synthetic esters from bio-based feedstocks). Designed for machinery in environmentally sensitive areas.

Advantages

- Rapidly biodegradable
- Non-toxic to aquatic life
- Renewable resource
- Excellent oiliness/lubricity
- High VI naturally

Limitations

- Poor oxidation stability (double bonds)
- Hydrolysis in presence of water
- High pour point (tropical oils)
- Higher cost vs mineral oils

Lubrication of Specific Machinery

Equipment	Lubricant Type	Key Requirement
Car engine	Multigrade oil (5W-30)	Wide temp range; detergency
Gear box	EP gear oil (GL-5)	High load; extreme pressure
Rolling bearing	Lithium grease	Low torque; water resistance
Hydraulic system	Hydraulic oil (ISO 46/68)	Good demulsibility; anti-wear
Turbines	Turbine oil	Excellent oxidation stability
Compressors	Compressor oil or PAG	Resist mixing with refrigerant
Food machinery	NSF H1 white oil	Non-toxic; food safe
Wire ropes	Bituminous compounds	Extreme pressure + corrosion resist

Numerical — Acid Value Determination

Formula

$$\text{Acid Value} = \frac{V \times M \times 56.1}{W} \quad \text{mg KOH / g oil}$$

where V = vol of KOH (mL), M = molarity of KOH, W = mass of oil (g), 56.1 = molar mass of KOH

Solved Example

2 g of oil titrated with 0.1 M KOH; 8.5 mL used to reach endpoint.

$$\text{AV} = \frac{8.5 \times 0.1 \times 56.1}{2} = \frac{47.685}{2} = \mathbf{23.84\ mg\ KOH/g}$$

(This is high; oil is significantly degraded and should be changed)

Unit 5 — PYQ Pattern Analysis

Topic	May 23	Nov 23	May 24
Viscosity + VI	7	3	7
Flash/Fire/Cloud/Pour point	7	7	3
Acid value + Saponification no.	3	7	7
Solid lubricants	3	3	3
Grease types	–	3	–
Mechanisms of lubrication	3	–	3
Classification of lubricants	–	–	7
Aniline point	3	3	3
Lubrication applications	3	–	–

Most likely 7-mark: Properties block (viscosity + VI + flash + fire + cloud + pour) **OR** acid value + saponification

Exam Tips — Unit 5: Lubricants

Do's

- State units for every property (cSt, mg KOH/g, °C)
- For acid value: mention significance (oil degradation)
- For saponification no.: mention what it measures (ester content)
- For VI: state high VI = better; mention why in engines
- For solid lubricants: distinguish graphite vs MoS_2 in vacuum

Don'ts

- Don't confuse acid value and saponification number
- Don't say graphite works in vacuum (it doesn't! MoS_2 does)
- Don't confuse flash point (momentary) and fire point (sustained)
- Don't say cloud point > pour point (cloud < pour, always)
- Don't write aniline point without stating rubber/seal implication

All Properties — At a Glance

Property	High Value	Low Value
Viscosity	Too thick; power loss	Too thin; film failure
VI	Good (less temp effect)	Poor (varies widely)
Flash point	Safer; no impurities	Dangerous; volatile impurities
Fire point	Safer	Dangerous
Cloud point	Waxes crystallize early	Good low-temp clarity
Pour point	Solid at low temp	Good for cold climate
Acid value	Degraded, corrosive	Fresh, good quality oil
Saponification no.	High fatty oil content	Mostly mineral oil
Aniline point	Paraffinic; rubber-safe	Aromatic; attacks rubber
Oiliness	Good boundary film	May need additives

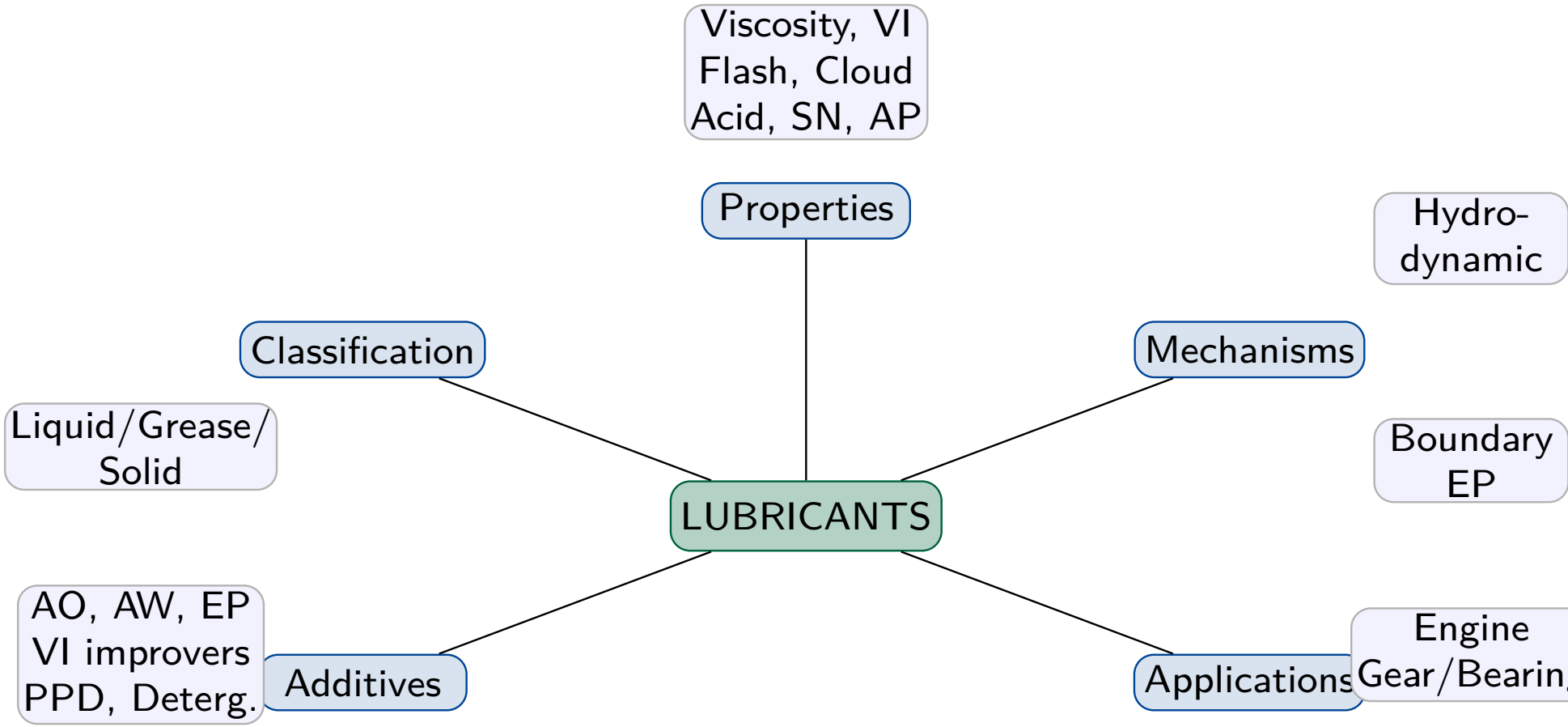
Unit 5 — Revision Numericals

1. Test oil at 40°C: U = 95 cSt; L = 150 cSt; H = 60 cSt. Calculate VI.
2. 3 g oil titrated with 0.05 M KOH, 12 mL used. Calculate acid value.
3. 5 g oil saponified with 25 mL of 0.5 M KOH; back-titrated with 0.5 M HCl; 8 mL required. Find SN.
   (SN = (vol KOH − vol HCl equivalent) × M × 56.1 / mass of oil)
4. An engine oil has flash point 180°C and fire point 200°C. State whether it is safe to use at 175°C. Justify.
5. Explain why MoS_2 is preferred over graphite for space applications.

Unit 5 — Revision Flash Points

Key Fact	Value / Rule
Acid value units	mg KOH / g oil
Saponification no. units	mg KOH / g oil
VI formula	$(L - U)/(L - H) \times 100$
Fire point $>$ Flash point	Always true
Cloud point $<$ Pour point	Always true
Graphite in vacuum	Does NOT work (needs vapour)
MoS_2 in vacuum	Works well
Grease $=$	Oil $+$ metallic soap $+$ additives
Li grease drop point	$\approx 190^\circ C$
Low aniline point	High aromatics; swells rubber

Unit 5 — Lubricants Mind Map



Unit 5 — Complete Summary

Topic	Core Outcome
Definition	Substance reducing friction, wear, heat between moving parts
Liquid lubricants	Mineral (paraffinic/naphthenic), vegetable, animal, synthetic
Greases	Oil + soap + additives; Li grease most versatile
Solid lubricants	Graphite (needs moisture); MoS_2 (vacuum OK)
Mechanisms	Hydrodynamic $\rightarrow$ mixed $\rightarrow$ boundary $\rightarrow$ EP
Viscosity + VI	Flow resistance; high VI = stable with temp
Flash/Fire point	Safety; detect impurities
Cloud/Pour point	Low-temp performance limits
Acid value	Oil degradation (oxidation) indicator
Saponification no.	Ester/fatty oil content
Aniline point	Aromaticity; rubber seal compatibility

Viscosity: Numerical Examples

Problem 1

Dynamic viscosity of oil $= 0.048$ Pa $\cdot$ s
Density $= 860$ kg/m^3

Find: Kinematic viscosity

Solution:

$$\nu = \frac{\eta}{\rho} = \frac{0.048}{860}$$

$$\nu = 5.58 \times 10^{-5} \text{ m}^2/\text{s}$$

$$= 55.8 \text{ cSt}$$

Problem 2

Kinematic viscosity at 40°C $= 95$ cSt
Kinematic viscosity at 100°C $= 11$ cSt

Compare to reference oil:
L (at 40°C for VI=0 oil) $= 140$ cSt
H (at 40°C for VI=100 oil) $= 65$ cSt

$$VI = \frac{L - U}{L - H} \times 100$$

$$= \frac{140 - 95}{140 - 65} \times 100 = \mathbf{60}$$

Key conversions: 1 Pa $\cdot$ s $= 1000$ mPa $\cdot$ s $= 1000$ cP; 1 m^2/s $= 10$ cSt; 1 cSt $= 1$ mm^2/s

Viscosity Index: ASTM Method Numerical

ASTM D2270 Method

Given: Oil viscosity at 40°C (U) = 72 cSt, at 100°C = 9.0 cSt
From ASTM tables for oils with viscosity 9.0 cSt at 100°C:
L = 119.0 cSt H = 56.0 cSt

Formula: $VI = \frac{L - U}{L - H} \times 100 = \frac{119 - 72}{119 - 56} \times 100$

$$VI = \frac{47}{63} \times 100 = \mathbf{74.6} \approx \mathbf{75}$$

Interpretation:

- VI = 75 → Medium quality
- VI > 100 → Multigrade/synthetic
- VI < 40 → Naphthenic (poor)

VI Ranges:

VI	Quality
<40	Low
40–80	Medium
80–110	High
>110	Very High

Grease Consistency: NLGI Classification

NLGI Grades

NLGI	Penetration	Consistency
000	445–475	Semi-fluid
00	400–430	Fluid
0	355–385	Very soft
1	310–340	Soft
2	265–295	Normal (most common)
3	220–250	Medium firm
4	175–205	Firm
5	130–160	Hard
6	85–115	Very hard

Penetration Test:
Depth (in 0.1mm) a standard cone sinks in 5 seconds at 25°C

NLGI 2 most used for:

- Wheel bearings
- Electric motor bearings
- General purpose

NLGI 0/1 for:

Centralized grease systems, cold climates

Lubricant Selection Guide

Application	Lubricant Type	Key Property
High-speed spindles	Low viscosity oil	Low friction
Heavy gear boxes	EP gear oil (ISO 320)	High load bearing
Wheel bearings	NLGI-2 grease	Water resistance
Cylinder walls	Cylinder oil	Film strength
High temperature ovens	Silicone grease	Thermal stability
Food processing	White mineral / PTFE	Non-toxic
Wire ropes	Graphite grease	Penetration
Hydraulic systems	HLP hydraulic oil	Anti-wear
Compressors	Comp. oil (ISO 46)	Low carbon deposit
High vacuum pumps	Diffusion pump oil	Very low vapour pressure

Rule of thumb:

Higher speed $\rightarrow$ lower viscosity; higher load $\rightarrow$ higher viscosity/EP additive

Extreme Pressure (EP) Additives: Detailed

How EP Additives Work

Under extreme load → metal-to-metal contact → local temperature spike

EP additives react with metal surface at high temp to form:

- **FeCl** (from Cl-compounds)
- **FeS / Fe S** (from S-compounds)
- **FePO** (from P-compounds)

Low shear strength layer → prevents welding/scuffing

Common EP Compounds

- **Cl:** Chlorinated paraffins (active >180°C)
- **S:** Dibenzyl disulfide, ZDDP
- **P:** Tricresyl phosphate (TCP)
- **S+P:** ZDDP — Zinc dialkyldithiophosphate (most versatile)

ZDDP also acts as antioxidant + antiwear

Biodegradable & Eco-Friendly Lubricants

Why Biodegradable?

- Mineral oils persist in environment 100s of years
- EU Ecolabel requires >60% biodegradation in 28 days
- Marine, forestry, agricultural applications

Types:

- **Vegetable oils:** Rapeseed (HEAR), sunflower, soy — rapidly biodegradable
- **Synthetic esters:** Polyol esters, diesters — high performance + biodegradable
- **PAG (Polyalkylene glycol):** Water soluble, low toxicity

Comparison

Property	Mineral	Bio-bas
Biodegradation	<30%	>60%
VI	95–110	150–22
Pour point	−15°C	−10 to −
Oxidation stability	Good	Fair
Cost	Low	High

Automotive Lubricants: Engine Oil Grades

SAE Viscosity Grades

Monograde: SAE 30, SAE 40 (summer only)
Multigrade: SAE 10W-40
10W = cold cranking at $-20°C$
40 = viscosity at $100°C$

Grade	Application
5W-30	Small cars, fuel economy
10W-40	Passenger cars (standard)
15W-40	Diesel engines, trucks
20W-50	Older engines, hot climate

API Service Classification

Gasoline engines (S-series):
SN/SP $\rightarrow$ latest; SM, SL $\rightarrow$ older

Diesel engines (C-series):
CK-4 $\rightarrow$ latest heavy duty

Additives in engine oil:

- Detergents (clean deposits)
- Dispersants (suspend soot)
- ZDDP (anti-wear)
- VI improvers (multigrade)
- Antioxidants

Industrial Gear Oils & Hydraulic Fluids

Industrial Gear Oils

ISO Grades: 68, 100, 150, 220, 320, 460, 680

Types:

- CLP (EP gear oil) — most common for enclosed gears
- HVI (high VI) — temperature variable applications
- SHC (synthetic) — extreme temp/load

Selection: higher speed→lower ISO grade; gear tooth sliding→EP additive

Hydraulic Fluids

ISO HM (anti-wear) and HLP (anti-wear+rust)

Key properties:

- Low compressibility
- Good VI (> 95)
- Anti-wear additives (ZDDP)
- Anti-foam agents
- Rust/oxidation inhibitors

Common grades: ISO 32, 46, 68

Fire-resistant fluids: HFA/HFB/HFC/HFD for mining

Previous Year Questions: Short Answer (Unit 5)

2-mark Questions:

1. Define viscosity index. What does a high VI indicate?
2. Distinguish flash point and fire point.
3. What is the role of EP additives?
4. Differentiate cloud point and pour point.
5. What is acid value of a lubricant?
6. Define saponification number.
7. State two functions of a lubricant.
8. What are solid lubricants? Give two examples.

3-mark Questions:

1. Explain hydrodynamic lubrication with diagram.
2. How is viscosity index measured?
3. Distinguish mineral and synthetic lubricants.
4. What is boundary lubrication? When does it occur?
5. Explain pourpoint depressants.
6. Compare grease and oil as lubricants.

Previous Year Questions: 7-Mark (Unit 5)

Descriptive Questions (7 marks each)

1. Explain in detail the various properties of lubricating oils with their significance. *(Flash pt, Fire pt, Cloud pt, Pour pt, VI, Aniline pt, Acid value)*
2. Describe the different mechanisms of lubrication. How does hydrodynamic lubrication differ from boundary lubrication?
3. What are synthetic lubricants? Discuss PAO, ester-type and silicone lubricants with advantages over mineral oils.
4. Classify lubricants. Explain greases — their composition, types and applications.
5. Discuss the role of various additives used in lubricating oils with examples.
6. Write a note on solid lubricants: graphite and MoS — structure, properties and applications.
7. Compare mineral oil, vegetable oil and synthetic lubricants on the basis of properties and applications.

Numericals Practice Set (Unit 5)

Practice Problems

Q1. Dynamic viscosity of oil $= 0.065$ Pa $\cdot$ s, density $= 890$ kg/m^3. Find kinematic viscosity in cSt.

Q2. U (at 40°C) $= 85$ cSt. L $= 125$ cSt, H $= 50$ cSt (ASTM table). Calculate Viscosity Index.

Q3. An oil has flash point 180°C and fire point 200°C. State significance of each.

Q4. Cloud point of oil A $= -10$°C, pour point $= -15$°C. Cloud point of oil B $= -5$°C, pour point $= -12$°C. Which oil is better for cold climate use?

Q5. 1 g of oil requires 2.5 mL of 0.1N KOH for neutralization. Find acid value.

Answers: Q1: 73.03 cSt Q2: VI $= 53.3$ Q3: Flash pt $\rightarrow$ fire hazard; fire pt $\rightarrow$ sustained combustion Q4: Oil A (lower pour pt) Q5: AV $= 2.5 \times 0.1 \times 56.1 / 1$ $= 14$ mg KOH/g

Common Exam Errors & Tips (Unit 5)

Common Mistakes

- Confusing flash point (vapour ignites momentarily) with fire point (sustained burning)
- Saying high VI = high viscosity (Wrong! VI = stability of viscosity with temperature)
- Cloud point > pour point (always cloud pt is higher)
- MoS acts as lubricant due to weak van der Waals between layers, NOT ionic bonds
- Saying all greases are soap + mineral oil — some use synthetic oil or non-soap thickeners

Scoring Tips

- Always define before explaining property
- Draw Stribeck curve for 7-mark lubrication mechanism Q
- For properties table Q: at least 6–7 properties with definition + significance
- Hydrodynamic lubrication: mention wedge film formation
- Grease Q: always mention thickener (soap) + base oil + additives
- EP lubricant: always mention chemical film formation at high temperature

Revision Flash Points: Unit 5 Key Facts

Property / Term	Key Fact
Viscosity units (dynamic)	Pa · s or cP (1 Pa · s = 1000 cP)
Viscosity units (kinematic)	m^2/s or cSt (1 m^2/s = 10 cSt)
High VI oil	Viscosity changes less with temperature
Flash point	Temp at which vapour momentarily ignites
Fire point	Temp at which oil sustains burning (>flash pt)
Cloud point	Temp at which wax crystals first appear
Pour point	Temp below which oil stops flowing (cloud pt > pour pt)
Acid value	mg KOH to neutralize 1 g oil (measures acidity)
Saponification No.	mg KOH to saponify 1 g oil (measures ester content)
NLGI 2 grease	Most common; penetration 265–295 × 0.1 mm
MoS lubricant	Layered hexagonal structure; weak van der Waals
Graphite lubricant	Good conductor; works in humid conditions
EP additives	Form sacrificial chemical film at

Lubricating Oil: Key Properties & Typical Values

Property	Typical Range	Significance
Viscosity @ 40°C	15–680 cSt	Film thickness; load carrying
Viscosity @ 100°C	3–100 cSt	High-temp performance
Viscosity Index	80–150+	Temp sensitivity of viscosity
Flash Point	150–320°C	Fire safety, volatility
Pour Point	−50 to −5°C	Cold start performance
Cloud Point	−40 to 0°C	Wax separation in cold
Acid Value	<0.1 (new oil)	Acidity/corrosiveness
Saponification No.	Varies	Ester content
Aniline Point	70–120°C	Aromatic content, rubber compatibility
Density @ 15°C	840–900 kg/m^3	Quality indicator

Used oil analysis monitors these values — significant change indicates degradation or contamination

Unit 5: Summary & Bridge to Unit 6

Unit 5 Covered

- ✓ Definition, functions, classification
- ✓ Liquid, semi-solid, solid lubricants
- ✓ Lubrication mechanisms (HD, EHD, boundary, EP)
- ✓ All key properties (viscosity, VI, flash/fire/cloud/pour pt, acid value, saponification No.)
- ✓ Additives: VI improvers, EP, antioxidants, detergents
- ✓ Automotive + industrial applications
- ✓ Biodegradable lubricants
- ✓ PYQ + numericals

Next: Unit 6 — Polymers

Topics Ahead:

- Polymer definition & classification
- Addition vs Condensation polymerization
- Thermoplastics vs Thermosets
- Important polymers: PE, PP, PVC, Nylon-66
- Elastomers: Natural rubber, Buna-S, Neoprene
- Conducting polymers: PANI
- Biodegradable polymers
- Fiber-reinforced composites

Unit 6: Polymers

Engineering Chemistry — DI01000071

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April 2, 2026

Polymer Definition · Polymerization · Thermoplastics & Thermosets
Elastomers · Conducting Polymers · Biodegradable Polymers

Unit 6 Overview: Polymers

Topics Covered

- Polymer definition & terminology
- Classification of polymers
- Addition polymerization
- Condensation polymerization
- Thermoplastics vs Thermosets
- Important thermoplastics
- Important thermosets (Bakelite, epoxy)
- Elastomers (natural & synthetic rubber)
- Conducting polymers
- Biodegradable polymers
- Fiber-reinforced composites

Exam Weightage

≈20% of paper
(Highest weightage unit)

Frequent PYQ topics:

- Nylon-66 synthesis
- Bakelite preparation (mechanism)
- Natural rubber vulcanization
- Buna-S / Neoprene structure
- Conducting polymers (PANI)
- Biodegradable polymers (PLA)

Polymer: Definition & Key Terms

Definitions

Polymer: Large molecule (macromolecule) formed by repetitive joining of small units

Monomer: Small repeating unit (e.g., ethene, vinyl chloride)

Degree of Polymerization (n): Number of repeat units in polymer chain

Repeat unit: Smallest structural unit that repeats

$M_n = n \times M_0$ (Mol. wt. of repeat unit)

Examples:

- Polyethylene: $n(-CH_2 - CH_2-)$ from ethene
- PVC: $n(-CH_2 - CHCl-)$ from vinyl chloride
- Nylon-66: from hexamethylene diamine + adipic acid

Functionality: Number of reactive sites per monomer

- Di-functional: linear polymer
- Tri-functional: cross-linked/branched

Classification of Polymers

Basis	Type	Examples
Source	Natural	Cellulose, starch, rubber, proteins
	Synthetic	PE, PVC, Nylon, Bakelite
Structure	Linear	HDPE, PVC, Nylon
	Branched	LDPE
	Cross-linked	Bakelite, vulcanized rubber
Thermal behavior	Thermoplastic	PE, PP, PVC, Nylon
	Thermoset	Bakelite, epoxy, polyester resin
Polymerization	Addition	PE, PVC, PTFE, polystyrene
	Condensation	Nylon, polyester, Bakelite
End use	Plastic, elastomer, fiber, coating	—

Addition Polymerization

Mechanism

Requires: Monomer with C=C double bond

Steps: (Chain growth)

1. **Initiation:** Free radical / ion attacks monomer
2. **Propagation:** Chain grows by successive addition
3. **Termination:** Radicals combine / disproportionate

No by-product formed

M_n can be very high (10^5–10^6)

Examples:

$n\mathrm{CH_2{=}CH_2} \xrightarrow{\Delta, P, \text{catalyst}} (-\mathrm{CH_2} - \mathrm{CH_2}-)_n$

Ethene $\rightarrow$ Polyethylene (PE)

$n\mathrm{CH_2{=}CHCl} \rightarrow (-\mathrm{CH_2} - \mathrm{CHCl}-)_n$

Vinyl chloride $\rightarrow$ PVC

$n\mathrm{CF_2{=}CF_2} \rightarrow (-\mathrm{CF_2} - \mathrm{CF_2}-)_n$

Tetrafluoroethylene $\rightarrow$ PTFE (Teflon)

Types: Free radical, cationic, anionic, coordination (Ziegler-Natta)

Condensation Polymerization

Mechanism

Requires: Bifunctional monomers (two reactive groups each)

Mechanism: (Step growth)
1. Two monomers react → dimer + by-product 2. Dimer reacts → tetramer + by-product 3. Continues until high MW polymer

By-products: H O, HCl, NH , CH OH
MW builds slowly

Example — Nylon-66:

$$n\mathrm{H_2N(CH_2)_6NH_2} + n\mathrm{HOOC(CH_2)_4COOH} \xrightarrow{-n\,\mathrm{H_2O}} (-\mathrm{NH(CH_2)_6NH–CO(CH_2)_4CO}-)_n$$

Hexamethylene diamine + Adipic acid → Nylon-66 + H O

Other examples:

- Nylon-6 (caprolactam ring opening)
- Polyester (diol + diacid)
- Bakelite (phenol + formaldehyde)

Thermoplastics vs Thermosets

Property	Thermoplastic	Thermoset
Structure	Linear/branched	3D cross-linked network
On heating	Softens/melts	Decomposes (burns)
Recyclable	Yes	No
Molding	Repeated	Only once
Solubility	Usually soluble	Insoluble
Strength	Moderate	Very high
Examples	PE, PP, PVC, Nylon	Bakelite, epoxy, urea-formaldehyde
Uses	Bottles, pipes, films	Electrical parts, laminates, adhesives

Thermoset mechanism:
Monomers cure via cross-linking $\rightarrow$ rigid, infusible network formed permanently

Common Thermoplastics:
LDPE, HDPE, PP, PVC, PS, Nylon-6, Nylon-66, PTFE, ABS, PET

Important Thermoplastics

Name	Monomer	Structure	Properties & Uses
LDPE	Ethene	Branched	Soft, flexible; polythene bags, films
HDPE	Ethene	Linear	Hard, rigid; pipes, bottles, containers
PP	Propene	Linear/isotactic	High mp (160°C), fatigue resistant; ropes, carpets
PVC	Vinyl chloride	Linear	Rigid/flexible; pipes, cables, floor tiles
Polystyrene (PS)	Styrene	Linear/atactic	Brittle, transparent; packaging foam
PTFE (Teflon)	TFE	Linear	Very low friction, chemical resistant; non-stick, gaskets
ABS	Acrylonitrile+ Butadiene+Styrene	—	Tough, impact resistant; helmets, appliances
PET	Ethylene glycol + TPA	Linear	Strong, transparent; PET bottles, polyester fibers

Polyethylene: LDPE vs HDPE

LDPE

Low Density Polyethylene

Process: High pressure (1000–3000 atm), 100–350°C, free radical

Structure: Highly branched (prevents close packing)

Density: 0.91–0.93 g/cm^3

Crystallinity: 50–60%

Properties: Soft, flexible, translucent

Uses: Cling film, carry bags, squeeze bottles, insulation

HDPE

High Density Polyethylene

Process: Low pressure (6–7 atm), Ziegler-Natta catalyst (TiCl + AlEt)

Structure: Linear (close packing possible)

Density: 0.94–0.97 g/cm^3

Crystallinity: 80–90%

Properties: Hard, rigid, translucent

Uses: Pipes, drums, bottles, chairs

Bakelite: Phenol-Formaldehyde Resin

Synthesis

Step 1: Phenol + HCHO (acid catalyst) $\rightarrow$ Novolac (linear, brittle)

Step 2: Novolac + more HCHO + hexamethylenetetramine $\rightarrow$ Bakelite

Mechanism:
Electrophilic substitution at ortho/para positions $\rightarrow$ methylene bridges form $\rightarrow$ 3D cross-linked network

Properties:

- Hard, brittle thermoset
- Excellent electrical insulator
- Heat resistant
- Chemical resistant
- Dark brown color

Uses:

- Electrical switches, plugs
- Radio cabinets (historical)
- Handles of pans & irons
- Laminates (Formica)
- Adhesives

Nylon-66: Synthesis & Properties

Synthesis of Nylon-66

Monomers:

Hexamethylenediamine: $H_2N(CH_2)_6NH_2$

Adipic acid: $HOOC(CH_2)_4COOH$

Reaction (Condensation):

$$n\,H_2N(CH_2)_6NH_2 + n\,HOOC(CH_2)_4COOH \xrightarrow{-nH_2O} [-NH(CH_2)_6NHCO(CH_2)_4CO-]_n$$

Properties:

- High tensile strength
- Abrasion resistant
- Good elasticity
- Low coefficient of friction
- Absorbs moisture

Uses:

- Textile fibers (stockings, fabrics)
- Ropes, bristles, brush fibers
- Gears, bearings (engineering)
- Parachute fabric

PVC & Teflon (PTFE)

PVC — Polyvinyl Chloride

$n CH_2{=}CHCl \rightarrow (-CH_2 - CHCl-)_n$

Unplasticized (UPVC): rigid, pipes, window frames
Plasticized (FPVC): flexible, cables, floor tiles, hoses

Properties: Flame retardant (Cl), cheap, corrosion resistant
Limitation: Releases HCl on burning (toxic)

PTFE — Teflon

$n CF_2{=}CF_2 \rightarrow (-CF_2 - CF_2-)_n$

Properties:

- Lowest COF of any solid (0.04)
- Heat resistant (260°C)
- Chemically inert (all acids/bases)
- Non-stick

Uses: Non-stick cookware, lab gaskets, seals, wire insulation

Natural Rubber: Structure & Properties

Natural Rubber

Source: Latex from *Hevea brasiliensis*

Chemical name: cis-1,4-Polyisoprene

Monomer: Isoprene ($CH_2{=}C(CH_3){-}CH{=}CH_2$)

Structure: Long coiled chains; cis configuration gives elasticity

Repeat unit: $(-CH_2 - C(CH_3){=}CH - CH_2-)_n$

Properties of Raw NR:

- Highly elastic
- Soft, tacky
- Poor tensile strength
- Affected by heat, cold, solvents
- Ages rapidly (oxidation/ozone)

Limitations requiring vulcanization:

- Becomes brittle in cold
- Sticky and soft in heat
- Dissolves in organic solvents

Vulcanization of Rubber

Vulcanization Process

Discovered by: Charles Goodyear (1839)

Process: Natural rubber + sulfur (3–5%) heated at 140–160°C

Mechanism: Sulfur forms cross-links (S–S bridges) between rubber chains at double bond positions

Rubber–S_x–Rubber cross-links

Hard rubber (ebonite): 30–50% sulfur

Effect of Vulcanization

Property	**Improvement**
Tensile strength	↑ greatly
Elasticity	Maintained
Hardness	↑
Chemical resistance	↑
Temp sensitivity	↓ (wider range)
Solvent resistance	↑

Synthetic Rubbers: Overview

Name	Monomers	Type	Properties & Uses
Buna-S (SBR)	Butadiene + Styrene (75:25)	Co-polymer	Good abrasion resistance; tyre treads
Buna-N (NBR)	Butadiene + Acrylonitrile	Co-polymer	Oil resistant; fuel hoses, gaskets
Neoprene (CR)	Chloroprene	Homopolymer	Weather, oil, flame resistant; industrial belts, wetsuits
Thiokol	Ethylene dichloride + Na polysulfide	Polysulfide	Oil/solvent resistant; rocket fuel binder, sealants
Butyl rubber (IIR)	Isobutylene + small isoprene	Co-polymer	Gas impermeable; inner tubes, stoppers
Silicone rubber	Dimethyldichlorosilane	Inorganic backbone	Wide temp range (-60 to 250°C); medical, aerospace

NR

dominates in tires (natural grip); SBR most produced synthetic rubber worldwide

Buna-S (SBR): Styrene-Butadiene Rubber

Synthesis

Monomers: Butadiene (75%) + Styrene (25%)

Process: Emulsion co-polymerization

Reaction:

$$n\mathrm{CH_2{=}CH{-}CH{=}CH_2} + n\mathrm{CH_2{=}CH{-}C_6H_5} \xrightarrow{\text{emulsion}} (-\mathrm{CH_2-CH{=}CH-CH_2-CH_2-CHC_6H_5}-)_n$$

Properties:

- Better abrasion resistance than NR
- Good aging resistance
- Less elastic than NR
- Good heat resistance

Uses:

- Automobile tyre treads (most common use)
- Shoe soles, belts
- Floor tiles, hoses

Note: Must be vulcanized for use

Neoprene & Buna-N

Neoprene (Polychloroprene)

Monomer: Chloroprene (2-chlorobutadiene)

$n CH_2{=}CCl{-}CH{=}CH_2$

$\rightarrow (-CH_2 - CCl{=}CH - CH_2-)_n$

Properties:

- Flame retardant (Cl atom)
- Oil & weather resistant
- Good tensile strength

Uses: Wetsuits, industrial belts, hoses, electrical cable jackets

Buna-N (NBR / Nitrile Rubber)

Monomers: Butadiene + Acrylonitrile (15–45% AN)

$(-CH_2 - CH{=}CH - CH_2 - CH_2 - CH(CN)-)_n$

Properties:

- Excellent oil & fuel resistance (CN groups)
- Poor weather resistance
- Good abrasion resistance

Uses: Fuel hoses, gaskets, O-rings, oil seals, gloves

Conducting Polymers: Introduction

What Are Conducting Polymers?

Conventional polymers are insulators ($\sigma < 10^{-12}$ S/cm)

Conducting polymers: σ up to 10^5 S/cm after doping

Conditions for conductivity:

- Conjugated double bonds (alternating C=C)
- Doping (oxidation/reduction introduces charge carriers)

Discovery: Shirakawa, MacDiarmid, Heeger (Nobel Prize 2000 — Chemistry)

Important Conducting Polymers:

- Polyacetylene (PA) — first, highest conductivity
- Polyaniline (PANI) — most studied, easy synthesis
- Polypyrrole (PPy) — good stability
- Polythiophene (PT)
- Poly(para-phenylene)

Doping types:

- p-type: oxidation (remove electrons)
- n-type: reduction (add electrons)

Polyaniline (PANI): Most Studied Conducting Polymer

Synthesis of PANI

Monomer: Aniline (C H NH)

Method: Chemical or electrochemical oxidation in acidic medium (HCl or H SO)

Oxidizing agent: (NH) S O (ammonium persulfate)

Reaction:

$n C_6H_5NH_2 \xrightarrow{\text{oxidation}}$ PANI (emeraldine salt)

Oxidation States:

- **Leucoemeraldine:** Fully reduced, white/colorless, insulating
- **Emeraldine base:** Half-oxidized, blue, insulating
- **Emeraldine salt:** Protonated, green, **conducting**
- **Pernigraniline:** Fully oxidized, violet, insulating

Uses: Anti-corrosion coatings, sensors, supercapacitors, EMI shielding, batteries

Biodegradable Polymers

Why Biodegradable?

Problem: Conventional plastics (PE, PP, PET) persist 100–500 years in environment

Solution: Polymers that degrade via microbial/enzymatic action

Degradation modes:

- Hydrolysis (ester, amide bonds)
- Microbial attack
- Photo-/thermo-oxidative degradation

Important Biodegradable Polymers:

- **PLA (Polylactic acid):** From corn starch; packaging, medical sutures
- **PGA (Polyglycolic acid):** Surgical sutures, dissolves in 2–4 weeks
- **PCL (Polycaprolactone):** Drug delivery, degrades in 2–4 years
- **PHB (Polyhydroxybutyrate):** Bacterial synthesis; packaging
- **Starch-based polymers:** Blends for bags/packaging

PLA: Polylactic Acid

Synthesis of PLA

Route 1: Direct condensation of lactic acid

$n\text{HO-CH(CH}_3\text{)-COOH} \rightarrow [-\text{O-CH(CH}_3\text{)-CO}-]_n + n\text{H}_2\text{O}$

Route 2: Ring-opening polymerization of lactide (cyclic dimer) — gives higher MW

Properties of PLA:

- Transparent, stiff
- Good tensile strength
- Degrades in industrial compost (6–12 months)
- Derived from renewable resources (corn, sugarcane)

Uses:

- Disposable packaging, cups, bags
- Medical: sutures, implants, drug delivery
- 3D printing filament (FDM)
- Agricultural films

Fiber-Reinforced Polymers (FRP) / Composites

What is FRP?

Composite = reinforcing fibers embedded in polymer matrix

Matrix (polymer): Epoxy, polyester, vinyl ester, nylon

Reinforcement:

- Glass fibers (GFRP) — most common
- Carbon fibers (CFRP) — high strength-to-weight
- Kevlar (aramid) — bullet-resistant
- Natural fibers (jute, sisal) — eco-friendly

Properties of FRP:

- High strength-to-weight ratio
- Corrosion resistant
- Design flexibility
- Good fatigue resistance

Applications:

- Aircraft fuselage, wings (CFRP)
- Boat hulls, storage tanks (GFRP)
- Wind turbine blades
- Sports equipment (bicycle frames, tennis rackets)
- Automotive body panels

Epoxy Resins

Synthesis

Most common: DGEBA (Diglycidyl ether of bisphenol A)

Bisphenol A + Epichlorohydrin $\xrightarrow{\text{NaOH}}$ Epoxy resin

Curing: Hardener (amine/anhydride) opens epoxide rings $\rightarrow$ 3D cross-linked thermoset

Mix ratio: Epoxy resin + curing agent (usually 2:1 or 1:1 by weight)

Properties:

- Excellent adhesion
- Chemical & moisture resistance
- Low shrinkage on curing
- Good electrical insulation
- High strength thermoset

Uses:

- Structural adhesives
- Circuit board laminates (FR4)
- Protective coatings/paints
- FRP matrix resin
- Encapsulation of electronics

Polymerization Methods: Comparison

Feature	Bulk	Solution	Emulsion
Medium	Monomer only	Monomer + solvent	Monomer + water + emulsifier
MW of product	High	Lower	Very high
Heat removal	Difficult	Easy (solvent)	Easy (water)
Purity	High	Solvent residue	Surfactant residue
Viscosity	Very high	Moderate	Low
Example	PMMA (cast acrylic), PVC	Solution SBR	SBR, NBR, PVC paste

Feature	Suspension	Notes
Medium	Monomer droplets in water + suspending agent	Bead polymer
MW	High	Good heat transfer
Product form	Beads	Easy separation
Example	Polystyrene beads, PVC suspension	

Glass Transition Temperature (T_g)

Definition

T_g: Temperature at which amorphous polymer transitions from glassy (rigid) to rubbery (flexible) state

Below T_g: Chains frozen, brittle, glassy
Above T_g: Chain mobility, rubbery, flexible

T_m: Melting point of crystalline region
Note: $T_g < T_m$ always

For rubber: $T_g <$ room temp (hence elastic)

Typical T_g values:

Polymer	**T_g (°C)**
Natural rubber	-73
Polybutadiene	-85
PVC (rigid)	$+87$
Polystyrene	$+100$
PMMA	$+105$
Polycarbonate	$+147$
Polyimide	$+300$
Nylon-66	$+57$
PET	$+67$

Polypropylene (PP) & Polystyrene (PS)

Polypropylene (PP)

$n CH_2{=}CHCH_3 \xrightarrow{\text{Z-N catalyst}} (-CH_2-CHCH_3-)_n$

Tacticity: Isotactic (commercial) — regular structure, crystalline

Properties: mp 160°C, strong, fatigue resistant (living hinge effect)

Uses: Food containers, bottle caps, ropes, carpets, car bumpers

Polystyrene (PS)

$n CH_2{=}CH{-}C_6H_5 \rightarrow (-CH_2-CH(C_6H_5)-)_n$

Types:

- GPPS: clear, brittle (CD cases)
- HIPS: impact-modified with rubber
- EPS (expanded): Thermocol — packaging foam

Properties: Rigid, transparent, brittle, cheap

Polyester & PET

Polyester (General)

Formation: Diol + Diacid $\xrightarrow{-H_2O}$ polyester

Linkage: –O–CO– (ester bond)

Alkyd resins: Polyester + oil (used in paints)

Unsaturated polyesters: Cross-linkable; used in FRP (GRP)

PET (Polyethylene Terephthalate)

Ethylene glycol + Terephthalic acid $\xrightarrow{-H_2O}$ $(-O-CH_2-CH_2-O-CO-C_6H_4-CO-)_n$

Properties: Transparent, strong, good barrier to O /CO

Uses:

- Water/soft drink bottles (most common)
- Polyester fibers (Dacron, Terylene)
- Magnetic tape base

Urea-Formaldehyde & Melamine Resins

Urea-Formaldehyde (UF)

Monomers: Urea + Formaldehyde (acid/base catalyst)

Product: Thermosetting resin, colorless/white

Properties:

- Harder than Bakelite
- Light-colored (can be made in any color)
- Good electrical insulation

Uses: Buttons, bottle caps, electrical fittings, plywood adhesive (UF glue)

Melamine Resin (MF)

Monomers: Melamine ($C_3H_6N_6$) + Formaldehyde

Properties:

- Very hard, scratch resistant
- Heat resistant (dishes, countertops)
- Good surface finish
- Self-extinguishing

Uses: Crockery (melamine dishes), Formica laminates, floor tiles, fire-retardant textiles

Mid-Point Summary: Unit 6

Covered So Far

- ✓ Polymer terminology & classification
- ✓ Addition polymerization (chain growth)
- ✓ Condensation polymerization (step growth)
- ✓ Thermoplastics vs Thermosets
- ✓ LDPE, HDPE, PP, PVC, PS, PTFE, PET
- ✓ Bakelite, epoxy, UF, melamine resins
- ✓ Natural rubber + vulcanization
- ✓ SBR, NBR, Neoprene (synthetic rubbers)

Still To Come

- Nylon-6 (caprolactam)
- Silicone polymers
- Applications comparison tables
- PYQ short & 7-mark questions
- Numericals / structural questions
- Exam tips & common errors
- Revision flash points
- Mind map & unit summary

Nylon-6 vs Nylon-66

Property	Nylon-6	Nylon-66
Monomer	Caprolactam (1 monomer)	Hexamethylene diamine + Adipic acid (2 monomers)
Polymerization	Ring-opening (caprolactam)	Condensation
Linkage	$-NH(CH_2)_5CO-$	$-NH(CH_2)_6NHCO(CH_2)_4CO-$
mp	220°C	265°C
Moisture absorption	Higher	Lower
Mechanical strength	Good	Slightly better
Processing	Easier	More difficult
Uses	Tire cords, fishing lines, bristles	Parachutes, gears, engineering parts
By-product	None	H O

Key fact: Both are polyamides (–CO–NH– linkage); named by carbon count in monomer(s)

Silicone Polymers (Polysiloxanes)

Structure & Synthesis

Backbone: Si–O–Si (siloxane) — inorganic; R groups on Si — organic

Monomer: Dimethyldichlorosilane $(CH_3)_2SiCl_2$

$(CH_3)_2SiCl_2 + H_2O \rightarrow (-Si(CH_3)_2-O-)_n + 2HCl$

Forms: Oils, greases, rubbers, resins

Unique Properties:

- Wide temperature range: $-60°C$ to $+250°C$
- Water repellent (hydrophobic)
- Biocompatible and non-toxic
- Good electrical insulation
- Outstanding weathering resistance
- Low surface tension

Uses: Medical implants, sealants, gaskets, cosmetics, release coatings, aerospace seals

Polymer Additives

Additive	Function	Examples
Plasticizers	Increase flexibility (lower T_g)	DOP (di-octyl phthalate) in PVC
Stabilizers	Prevent degradation by heat/UV	Ca/Zn stearates, HALS
Antioxidants	Prevent oxidative degradation	Hindered phenols, phosphites
Fillers	Reduce cost, improve stiffness	CaCO , talc, silica, carbon black
Flame retardants	Reduce flammability	Brominated compounds, Al(OH)
Colorants	Pigments/dyes	TiO (white), carbon black
Lubricants	Easy mold release, better flow	Stearic acid, wax
Reinforcing agents	Improve mechanical properties	Glass fibers, carbon fibers, clay

Note:

Modern polymer products always contain several additives — pure polymer is rarely used directly

Recycling of Polymers

Recycling Codes (Resin ID)

Code	Polymer	Common Use
1	PET	Water bottles
2	HDPE	Milk jugs, pipes
3	PVC	Pipes, cables
4	LDPE	Cling films, bags
5	PP	Containers, caps
6	PS	Foam cups, trays
7	Others	Polycarbonate, ABS

Types of Recycling:

- **Mechanical:** Melt and re-process (thermoplastics only)
- **Chemical:** Depolymerize back to monomers (PET $\rightarrow$ ethylene glycol + TPA)
- **Energy recovery:** Incineration with heat recovery
- **Biodegradation:** PLA composting

Thermosets cannot be mechanically recycled — only ground for filler or energy recovery

Rubber Compounding

What is Rubber Compounding?

Mixing of raw rubber with various ingredients before vulcanization

Ingredients added:

- **Vulcanizing agent:** Sulfur (2–5%)
- **Accelerator:** MBT, CBS (speeds vulcanization)
- **Activator:** ZnO + stearic acid
- **Antioxidant:** Phenyl-β-naphthylamine
- **Filler:** Carbon black (reinforces 3–4$\times$ strength)
- **Plasticizer:** PE wax (for processability)

Importance of Carbon Black:
Carbon black (15–35 phr) is the single most important rubber reinforcing filler:

- Increases tensile strength 3–4$\times$
- Improves abrasion resistance
- Used in ALL tire compounds

Hard rubber (Ebonite):
30–50% sulfur $\rightarrow$ fully crosslinked, rigid, used for bowling balls, battery cases

Copolymers & Polymer Blends

Copolymers

Polymer chain from **two or more** different monomers

Types:

- **Random:** –A-B-A-A-B-B-A– (SBR)
- **Alternating:** –A-B-A-B-A-B–
- **Block:** –AAAA-BBBB– (SBS thermoplastic elastomer)
- **Graft:** Main A chain with B branches (HIPS)

Properties tunable between two homopolymers

Polymer Blends

Physical mixture of $\geq$ 2 polymers (like alloys)

Miscible: Homogeneous (rare) — PS/PPO
Immiscible: Phase-separated (most)

Examples:

- ABS = acrylonitrile + butadiene + styrene blend/copolymer
- PC/ABS blend — dashboards
- Nylon/rubber blends — toughened nylon

Smart & Special-Purpose Polymers

Shape Memory Polymers (SMP):
Return to original shape on heating above T_g
Uses: Medical stents, deployable structures

Hydrogels:
Cross-linked hydrophilic networks that absorb large amounts of water
Uses: Contact lenses, drug delivery, wound dressings, superabsorbent diapers

Ion Exchange Resins:
Sulfonated PS (cation exchanger) or quaternary amine PS (anion exchanger)
Uses: Water softening, deionization, chromatography

Liquid Crystal Polymers (LCP):
Rigid-rod chains with ordered structure; high strength at low weight
Uses: Electronics connectors, aircraft parts

Piezoelectric Polymers:
PVDF — generates voltage on deformation
Uses: Pressure sensors, transducers

Photoresists:
UV-sensitive polymers used in semiconductor lithography (PMMA, novolac + diazonaphthoquinone)

Important Polymers: Properties Summary

Polymer	Type	Mono.	mp/Tg	Key Use
HDPE	TP, addition	Ethene	130°C	Pipes, drums
LDPE	TP, addition	Ethene	110°C	Bags, films
PVC	TP, addition	Vinyl Cl	87°C(Tg)	Pipes, cables
PP	TP, addition	Propene	160°C	Ropes, containers
PTFE	TP, addition	TFE	327°C	Non-stick, seals
Nylon-66	TP, cond.	HDA+AA	265°C	Fibers, gears
PET	TP, cond.	EG+TPA	260°C	Bottles, fibers
Bakelite	TS, cond.	P+HCHO	—	Electrical parts
Epoxy	TS, add.	BPA+ECH	—	Adhesives, FRP
NR (vulc.)	Elastomer	Isoprene	−73(Tg)	Tyres
SBR	Elastomer	Bu+Sty	−60(Tg)	Tyre treads

TP=thermoplastic, TS=thermoset, cond.=condensation, HDA=hexamethylene diamine, AA=adipic acid, EG=ethylene glycol, TPA=terephthalic acid, P=phenol, BPA=bisphenol A, ECH=epichlorohydrin

PYQ Pattern Analysis: Unit 6 Polymers

Frequently Asked Topics

Almost every year (7-mark):

- Nylon-66: monomers, reaction, structure, properties, uses
- Bakelite: preparation mechanism (novolac $\rightarrow$ resole $\rightarrow$ Bakelite), properties, uses
- Natural rubber: structure, limitations, vulcanization (process + effect), uses

Alternate years (7-mark):

- Buna-S: monomers, structure, properties, uses vs NR
- PLA or biodegradable polymers: need, synthesis, types, significance
- Conducting polymers: PANI — synthesis, doping, uses

Short questions frequently:
Classification of polymers, distinguish addition vs condensation, thermoplastic vs thermoset, T_g definition

Previous Year Questions: Short Answer (Unit 6)

2-mark Questions:

1. Define polymer. Give two examples of addition polymers.
2. Distinguish thermoplastic and thermoset with examples.
3. What are biodegradable polymers? Give two examples.
4. Define glass transition temperature (T_g).
5. What is vulcanization? State its effect on natural rubber.
6. What is degree of polymerization?
7. Distinguish addition and condensation polymerization.
8. What are conducting polymers?

3-mark Questions:

1. Describe the preparation and uses of Teflon (PTFE).
2. Explain the synthesis of PET.
3. What are fiber-reinforced composites? Give uses.
4. Explain the doping mechanism in PANI.
5. Compare Nylon-6 and Nylon-66.
6. What are elastomers? Give three examples.

Previous Year Questions: 7-Mark (Unit 6)

Descriptive Questions (7 marks each)

1. Explain the preparation, properties and uses of Nylon-66. Write the repeat unit structure.
2. Describe the formation of Bakelite from phenol and formaldehyde. Give its properties and uses.
3. Explain the structure of natural rubber. What are its limitations? How does vulcanization overcome them?
4. What is Buna-S? Write the monomers, polymerization reaction, and compare its properties with natural rubber.
5. What are conducting polymers? Explain polyaniline (PANI) with its synthesis, oxidation states and applications.
6. Classify polymers. Explain addition and condensation polymerization with suitable examples and distinguish between them.
7. Write a note on: (a) Biodegradable polymers (b) Fiber-reinforced composites.

Structural Questions: Write Repeat Units

Write repeat unit of:

1. **Polyethylene (PE)**
$(-CH_2 - CH_2-)_n$
2. **PVC**
$(-CH_2 - CHCl-)_n$
3. **Polystyrene**
$(-CH_2 - CH(C_6H_5)-)_n$
4. **PTFE**
$(-CF_2 - CF_2-)_n$
5. **Natural rubber (cis-polyisoprene)**
$(-CH_2 - C(CH_3)=CH - CH_2-)_n$

Write repeat unit of:

6. **Nylon-66**
$(-NH(CH_2)_6NHCO(CH_2)_4CO-)_n$
7. **Neoprene**
$(-CH_2 - CCl=CH - CH_2-)_n$
8. **Buna-N (NBR)**
$(-CH_2CH=CHCH_2 - CH_2CH(CN)-)_n$
9. **PET**
$(-O\text{-}CH_2CH_2\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO-)_n$
10. **Silicone**
$(-Si(CH_3)_2\text{-}O-)_n$

Numericals: Degree of Polymerization & MW

Solved Examples

Q1. Calculate MW of nylon-66 if degree of polymerization = 200.
Repeat unit: $-[NH(CH_2)_6NHCO(CH_2)_4CO]-$
$M_0 = 6(14) + 2(14) + 2(14) + 2(16 + 12) = 226$ g/mol
$M_n = 200 \times 226 = 45{,}200$ g/mol

Q2. MW of PVC sample = 125,000 g/mol. Find degree of polymerization.
M_0 of repeat unit $(-CH_2 - CHCl-) = 62.5$ g/mol

$$n = \frac{125000}{62.5} = 2000$$

Q3. How many monomer units in polyethylene of MW = 56,000 g/mol?
M_0 of $(-CH_2 - CH_2-) = 28$ g/mol; $n = 56000/28 = \mathbf{2000}$

Common Exam Errors & Tips (Unit 6)

Common Mistakes

- Calling Nylon-66 an addition polymer (it is condensation — amide bond with H O loss)
- Drawing cis-isoprene as trans (must be cis for elastic properties)
- Saying all rubbers are natural (SBR/NBR/Neoprene are synthetic)
- Confusing Buna-S (75% butadiene) with Buna-N (butadiene + acrylonitrile)
- PTFE is addition polymerization (not condensation — no by-product)

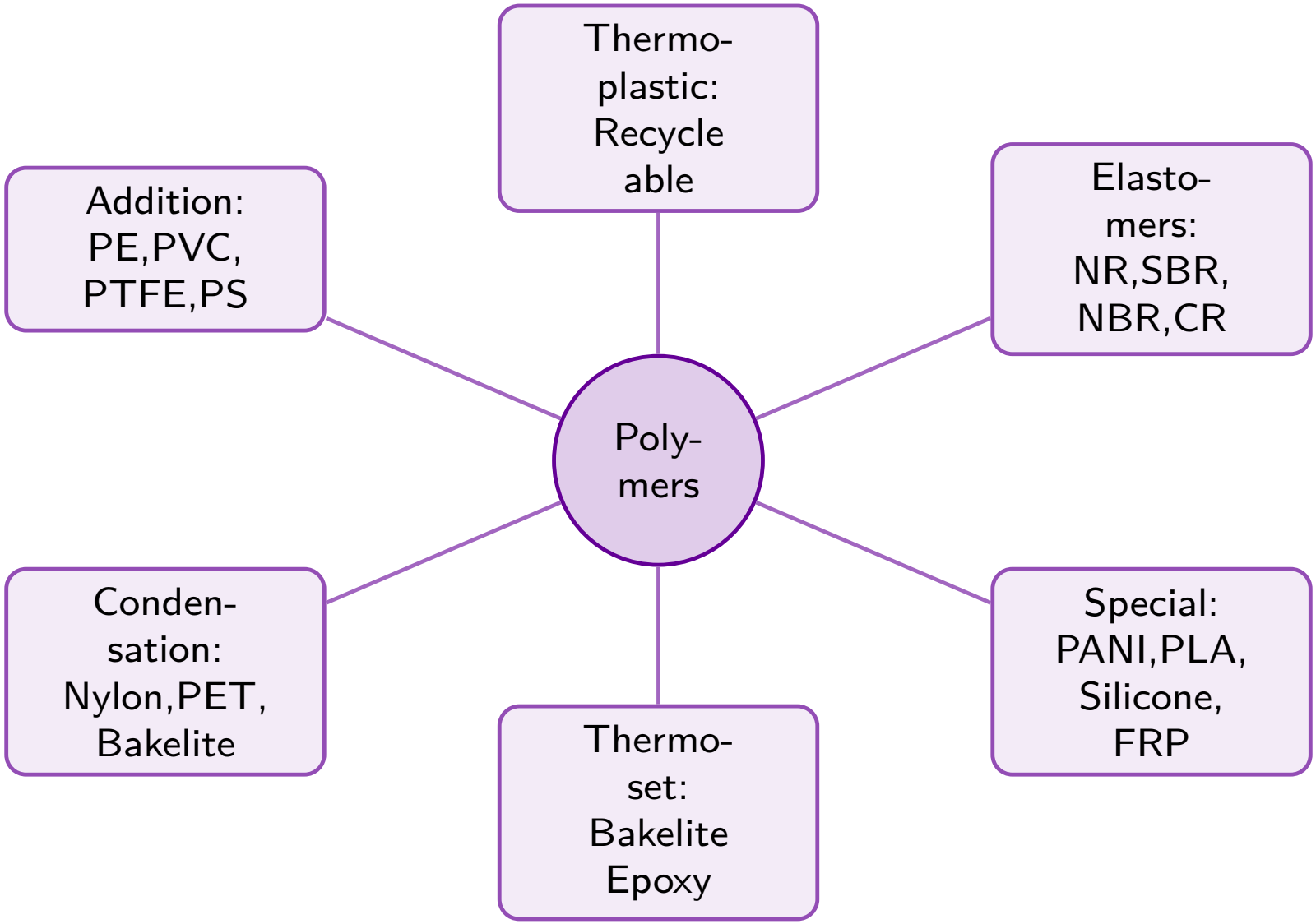
Exam Scoring Tips

- For Bakelite: always describe mechanism (electrophilic substitution) + draw cross-linked structure
- For vulcanization: state % sulfur, temp, duration, and draw S–S bridges
- For Nylon-66: always write both monomers + balanced equation
- Mention trade names where known (Teflon, Terylene, Neoprene)
- 7-mark answers: definition → synthesis/structure → properties → uses (5+ uses)

Revision Flash Points: Unit 6 Key Facts

Term / Polymer	Key Fact
Addition polymerization	No by-product; requires C=C in monomer
Condensation polymerization	By-product (H O, HCl, etc.); bi-functional monomers
LDPE vs HDPE	LDPE: branched, soft; HDPE: linear, rigid
Nylon-66 monomers	HDA (6C amine) + Adipic acid (6C diacid)
Nylon-66 linkage	Amide bond (–CO–NH–); by-product = H O
Bakelite	Phenol + HCHO; thermoset; 3D cross-linked
Natural rubber	cis-1,4-polyisoprene, from Hevea brasiliensis
Vulcanization agent	Sulfur (3–5%); 140–160°C; forms S–S bridges
Buna-S components	75% butadiene + 25% styrene
PANI conducting form	Emeraldine salt (protonated)
PLA degradation	Compostable in 6–12 months (industrial)
T_g of NR	−73°C (well below RT → elastic at room temp)
Nobel Prize 2000	Shirakawa, MacDiarmid, Heeger

Unit 6: Polymers — Mind Map



Polycarbonate (PC)

Synthesis

Monomers: Bisphenol A + Phosgene ($COCl_2$)

$$HO\text{-}C_6H_4\text{-}C(CH_3)_2\text{-}C_6H_4\text{-}OH + COCl_2 \xrightarrow{-2HCl} (-O\text{-BPA-}O\text{-}CO-)_n$$

Alternative: Interfacial polycondensation or melt transesterification

Outstanding Properties:

- Optically transparent
- Impact strength $\sim$250$\times$ glass
- $T_g = 147°C$ (high heat resistance)
- Dimensional stability
- Good electrical insulation

Uses:

- Bullet-proof glass (laminated)
- CDs, DVDs, Blu-ray discs
- Eyeglass lenses
- Helmets, shields
- Greenhouse panels

Polyacetylene: The First Conducting Polymer

Polyacetylene (PA)

Monomer: Acetylene (HC CH)

$$n\mathrm{HC}{\equiv}\mathrm{CH} \xrightarrow{\text{Ziegler-Natta}} (-\mathrm{CH}{=}\mathrm{CH}-)_n$$

Forms:
cis-PA (silvery, less stable)
trans-PA (golden, more stable)

Doping: I (p-type) or Na/K (n-type)
Conductivity: up to 10^5 S/cm (metallic!)

Band Theory Explanation:
Alternating single-double bonds $\rightarrow$ conjugated π system $\rightarrow$ overlapping p-orbitals $\rightarrow$ delocalized electrons

Undoped PA: semiconductor
Doped PA: conductor (removes/adds electrons from π band)

Limitations:

- Air-sensitive (oxidizes rapidly)
- Insoluble and infusible
- Difficult to process

Hence PANI preferred for practical use

Polymer Applications by Field

Field	Polymer	Application
Packaging	LDPE, PET, PP	Bags, bottles, wraps, trays
Construction	PVC, epoxy, FRP	Pipes, coatings, structural panels
Automotive	ABS, PP, Nylon, SBR	Dashboards, bumpers, tires
Medical	PTFE, silicone, PGA, PLA	Implants, sutures, drug delivery
Electronics	PC, epoxy, PTFE	Circuit boards, connectors, insulation
Textiles	Nylon-66, PET (Terylene)	Fabrics, ropes, sportswear
Aerospace	CFRP, Kevlar, PEEK	Fuselage, structural components
Agriculture	LDPE, PLA film	Mulch films, greenhouse covers
Consumer goods	PS, PP, ABS, PC	Appliances, toys, housewares

Natural Rubber vs Synthetic Rubber

Property	Natural Rubber	Synthetic (SBR)
Source	Hevea brasiliensis (botanical)	Petrochemical (butadiene+styrene)
Chemical name	cis-1,4-Polyisoprene	Styrene-Butadiene Rubber
Elasticity	Excellent	Good (less than NR)
Tensile strength (unfilled)	Very high	Lower
Abrasion resistance	Moderate	Better than NR
Heat resistance	Poor	Better
Oil resistance	Poor	Poor (NBR needed for oil)
Weather/ozone resistance	Poor	Moderate
Cost	Higher (variable)	Lower, consistent supply
Vulcanization	Required	Required
Main uses	Aircraft tyres, surgical gloves	Car tyre treads (70% market)

Polymer Degradation & Aging

Types of Degradation

Thermal: Chain scission/oxidation at high temp; poly(MMA) depolymerizes cleanly

Oxidative: O /ozone attacks double bonds in rubbers → cracking

Photo (UV): UV breaks C–C bonds; chalking/yellowing of PP, PVC

Hydrolytic: Water cleaves ester/amide bonds; affects PET, nylon

Biological: Microbes degrade bio-based polymers (PLA, PHB)

Mechanical: Fatigue, wear, stress cracking

Stabilization Strategies:

- UV stabilizers (HALS) — absorb/quench UV energy
- Antioxidants — interrupt radical chain oxidation
- Heat stabilizers (Ca/Zn) — prevent HCl elimination in PVC
- Ozone protectants — wax bloom on rubber surface
- Carbon black — UV screen in HDPE pipes

Service life prediction: Arrhenius model; accelerated aging tests at elevated temp

Other Conducting Polymers: PPy & PT

Polypyrrole (PPy)

Monomer: Pyrrole (5-membered N-heterocycle)

Synthesis: Electrochemical or chemical oxidation (FeCl)

Properties:

- $\sigma \approx$ 100–200 S/cm (doped)
- Good environmental stability
- Biocompatible

Uses: Sensors, actuators, corrosion protection, supercapacitors

Polythiophene (PT)

Monomer: Thiophene (5-membered S-heterocycle)

Important derivative: PEDOT (poly 3,4-ethylenedioxythiophene)

PEDOT:PSS:

- σ up to 1000 S/cm
- Transparent conducting film
- Solution processable

Uses: Organic solar cells (OPV), OLEDs, transparent electrodes, anti-static coatings

Nanocomposites: Polymers + Nanomaterials

Polymer Nanocomposites:
Dispersing nanoscale fillers (<100 nm) in polymer matrix → dramatic property improvements at low loading (1–5%)

Common nanofillers:

- **Nanoclay:** montmorillonite (MMT) → barrier, flame retardancy
- **Carbon nanotubes (CNT):** conductivity, strength
- **Graphene:** barrier, conductivity, mechanical
- **Nano-SiO , nano-TiO :** UV protection, scratch resistance

Why Nano?

High surface area: Nano fillers have aspect ratio >100 → more interface with matrix

Key applications:

- Nylon-6/clay nanocomposite (Toyota, 1990s) — first commercial nanocomposite; engine parts
- CNT-polymer: EMI shielding, lightweight structural
- Graphene-PE: gas barrier packaging

Environmental Impact of Plastics

Problems

- **Persistence:** PE/PP last 400–500 years in soil
- **Microplastics:** Fragments <5 mm enter food chain; found in oceans, drinking water, human blood
- **Marine pollution:** 8 million tonnes plastic/year enter oceans
- **Toxic additives:** Phthalate plasticizers, BPA (endocrine disruptors) leach from PVC, PC
- **Incineration:** HCl from PVC, dioxins from Cl-plastics

Solutions:

- Biodegradable polymers (PLA, PHB)
- Mechanical recycling (PET, HDPE)
- Chemical recycling (pyrolysis, glycolysis)
- Extended producer responsibility (EPR)
- Single-use plastic bans (EU, India)
- Bio-based feedstocks (sugarcane PE, bio-PET)

India context: Ban on single-use plastics <75 micron effective July 2022

More PYQ Short Answer Practice (Unit 6)

Answer in 2–3 lines:

1. Why is LDPE softer than HDPE?
2. Why does natural rubber become brittle in cold and sticky in heat?
3. What is the role of sulfur in vulcanization?
4. Why is Bakelite called a thermosetting polymer?
5. What property makes PTFE non-stick?
6. Why are biodegradable polymers preferred for medical sutures?
7. Distinguish Neoprene and Buna-N based on oil resistance.
8. Why is cis-configuration important in natural rubber?

Model Answers:

1. LDPE has branched chains $\rightarrow$ less crystallinity $\rightarrow$ softer
2. $T_g < -70°C \rightarrow$ chains mobile at RT; heat $\rightarrow$ chains too mobile, flow
3. Sulfur forms S–S crosslinks between chains, restricting slippage
4. Once set (cured), 3D network cannot melt — only decomposes
5. Extremely low surface energy C–F bonds adsorb nothing
6. PGA/PLA degrade inside body $\rightarrow$ no removal surgery needed
7. NBR (nitrile groups) oil-resistant; Neoprene weather/flame resistant but not oil

Additional Numericals (Unit 6)

Practice Problems

Q1. A sample of polystyrene has MW = 104,000 g/mol. Find degree of polymerization.
*(Repeat unit $-CH-CH(C_6H_5)-$: $M_0 = 104$ g/mol; $n = 104{,}000/104 =$ **1000**)*

Q2. Nylon-66 has $n = 150$. Calculate MW of polymer.
*($M_0 = 226$ g/mol; $MW = 150 \times 226 =$ **33,900 g/mol**)*

Q3. What mass of adipic acid is needed to produce 10 g of Nylon-66? (MW of Nylon-66 repeat unit = 226; MW of adipic acid = 146)
1 mol repeat unit requires 1 mol adipic acid
moles of RU = 10/226 = 0.0443 mol
*mass of adipic acid = $0.0443 \times 146 =$ **6.47 g***

Q4. PET repeat unit MW = 192 g/mol. Find n for PET of MW = 96,000 g/mol.
*$n = 96000/192 =$ **500***

Polymer Processing Methods

Process	Polymer Type	Products
Injection molding	Thermoplastics	Caps, toys, housings, car parts (high volume)
Extrusion	Thermoplastics	Pipes, sheets, films, profiles (continuous)
Blow molding	Thermoplastics	Hollow bottles (PET, HDPE, PP)
Compression molding	Thermosets	Bakelite parts, rubber gaskets
Reaction injection molding (RIM)	Thermosets (polyurethane)	Car bumpers, foam seats
Rotational molding	Thermoplastics	Large tanks, playground equipment
Fiber spinning	Nylon, PET, PP	Textile fibers, industrial yarns
Calendering	PVC	Sheet, floor tiles, artificial leather

Polyurethane & Acrylic Polymers

Polyurethane (PU)

Linkage: urethane (−NH−CO−O−)

Polyol + Diisocyanate → PU

Forms:

- Flexible foam (furniture, mattresses)
- Rigid foam (insulation panels)
- Elastomeric (spandex/Lycra fibers)
- Coatings, adhesives

Acrylic Polymers

PMMA (Perspex/Lucite):

$n\mathrm{CH}=\mathrm{C}(\mathrm{CH})\mathrm{COOCH} \rightarrow \mathrm{PMMA}$

- Optically clear (better than glass)
- UV resistant, lightweight
- **Uses:** Acrylic glass, aquariums, signs, aircraft canopies

Polyacrylonitrile (PAN):

- Carbon fiber precursor
- Acrylic fibers (Orlon)

Bio-based & Future Polymers

Bio-based but not biodegradable:

- Bio-PE (from sugarcane ethanol $\rightarrow$ ethylene)
- Bio-PET (30% bio-based MEG from sugarcane)
- Bio-based drop-in replacements — same properties, renewable source

PHB/PHBV (PHA family):
Produced by bacteria (Cupriavidus necator)
Truly biodegradable in soil/marine environments

High cost $\rightarrow$ limited commercial use currently

Emerging Technologies

- **Covalent adaptable networks (CANs):** Thermosets that can be reprocessed (vitrimer)
- **Self-healing polymers:** Repair cracks autonomously (Diels-Alder reversible bonds)
- **4D printing:** Shape memory polymer + 3D printing
- **Protein-based polymers:** Spider silk, elastin mimetics — extremely high toughness

Unit 6: Key Properties & Values for Exam

Fact	Value / Detail
Nylon-66 mp	265°C
NR vulcanization	Sulfur 3–5%, 140–160°C, S–S bridges
Buna-S ratio	75% butadiene : 25% styrene
PTFE coefficient of friction	0.04 (lowest of any solid)
PLA degradation time	6–12 months (industrial composting)
PC impact strength	$\sim$250$\times$ ordinary glass
Nobel Prize (conducting polymers)	2000 — Shirakawa, MacDiarmid, Heeger
PANI conducting form	Emeraldine salt (green, protonated)
Carbon black in rubber	Increases tensile strength 3–4$\times$
Degree of polymerization	$n = M_n/M_0$
Thermoset recycling	Not possible (only comminuted for filler)
Bakelite color	Dark brown/black (phenol condensation products)
Nylon type linkage	Amide ($-$CO$-$NH$-$)
PET bottle recycling code	1 (PETE)

Unit 6: Summary & Bridge to Unit 7

Unit 6 Covered

- ✓ Polymer terminology & classification
- ✓ Addition & condensation polymerization
- ✓ Thermoplastics: PE, PP, PVC, PTFE, PS, PC, PET
- ✓ Thermosets: Bakelite, epoxy, UF, melamine
- ✓ Elastomers: NR, vulcanization, SBR, NBR, Neoprene
- ✓ Conducting polymers: Polyacetylene, PANI, PPy
- ✓ Biodegradable: PLA, PGA, PHB

Next: Unit 7 — Water

Topics Ahead:

- Water quality parameters (DO, BOD, COD)
- Hardness of water: types & units
- Softening methods (lime-soda, zeolite, ion exchange)
- Reverse osmosis & membrane processes
- Boiler feed water treatment
- Desalination
- Sewage/wastewater treatment
- Drinking water treatment

Unit 7: Water

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April 2, 2026

Water Quality · Hardness · Softening Methods
Boiler Feed Water · Desalination · Wastewater Treatment

Unit 7 Overview: Water

Topics Covered

- Water quality parameters
- DO, BOD, COD
- Hardness: types, units, causes
- Lime-soda process
- Zeolite/Permutit process
- Ion exchange process
- Reverse osmosis
- Boiler feed water treatment
- Desalination methods
- Municipal water treatment
- Sewage treatment

Exam Weightage

≈15% of paper

Frequently asked:

- Hardness numericals (ppm, mg/L, °F, °Cl)
- Lime-soda process reactions
- Zeolite process (regeneration)
- BOD vs COD distinction
- Reverse osmosis principle
- Boiler troubles (scale, priming)
- Drinking water treatment flowchart

Water Quality Parameters

Physical Parameters

- **Turbidity:** Suspended particles scattering light (NTU); drinking water <1 NTU
- **Color:** True (dissolved) vs apparent (suspended); Hazen units
- **Odour & taste:** H S (rotten egg), algal metabolites
- **Temperature:** Affects DO, reaction rates, aquatic life
- **TDS:** Total Dissolved Solids (mg/L); drinking water <500 mg/L

Chemical Parameters

- **pH:** 6.5–8.5 for drinking water
- **Hardness:** Ca^{2} , Mg^{2} content (mg/L as CaCO)
- **Alkalinity:** OH , CO ^{2} , HCO content
- **Chloride:** <250 mg/L (taste threshold)
- **Nitrate:** <45 mg/L (infant methemoglobinemia risk)
- **Fluoride:** 0.6–1.5 mg/L (dental health)

DO, BOD and COD

Dissolved Oxygen (DO)

DO: Amount of O dissolved in water
Saturation: $\sim$9 mg/L at 20°C, 1 atm

Significance:

- $>$6 mg/L: good for fish
- $<$4 mg/L: stressed aquatic life
- $<$1 mg/L: anaerobic (septic)

Reduced by: high temp, organic pollution, algal decay

BOD (Biochemical Oxygen Demand):
O consumed by microbes to decompose organic matter in water at 20°C in 5 days (BOD)
High BOD $\rightarrow$ high pollution
Clean water: $<$1 mg/L; sewage: 200–400 mg/L

COD (Chemical Oxygen Demand):
O equivalent of all oxidisable matter (organic + inorganic) using K Cr O
COD $>$ BOD always
Measures total oxidisable load faster (2 hrs vs 5 days)

BOD/COD ratio: $>$0.6 $\rightarrow$ biodegradable waste

Hardness of Water: Definition & Types

Definition

Hardness: Property of water that prevents lathering with soap and causes scale in boilers

Caused by: Dissolved salts of Ca^2 and Mg^2

Soap reaction:
$2RCOONa + CaCl_2 \rightarrow (RCOO)_2Ca \downarrow + 2NaCl$
(scum/curd formed — waste of soap)

Types of Hardness:

Temporary hardness:
Caused by $Ca(HCO$) , $Mg(HCO$)
Removed by boiling:
$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2$

Permanent hardness:
Caused by $CaCl$, $MgCl$, $CaSO$, $MgSO$
Not removed by boiling
Removed by chemical/ion exchange methods

Total hardness = Temporary + Permanent

Units of Hardness & Interconversion

Hardness Units

ppm (mg/L): mg of CaCO equivalent per litre

Degree French (°F): 1°F = 10 mg CaCO /L

Degree Clark (°Cl): 1°Cl = 14.3 mg CaCO /L

Degree German (°d): 1°d = 17.8 mg CaCO /L

Equivalence:
1°Cl = 1.43°F = 0.8°d

Conversion to CaCO equivalents:

$$\text{Hardness (ppm)} = \frac{\text{Amount of salt (mg/L)} \times 100}{\text{Mol. wt. of salt}}$$

Example:

CaSO = 68 mg/L; MW = 136

$$\text{Hardness} = \frac{68 \times 100}{136} = 50 \text{ ppm}$$

Unit classification:

Soft	<75	ppm
Moderately hard	75–150	ppm
Hard	150–300	ppm
Very hard	>300	ppm

Hardness Numerical: Worked Example

Problem

Water contains: $Ca(HCO_3)_2$ = 16.2 mg/L, $MgCl_2$ = 19 mg/L, $CaSO_4$ = 13.6 mg/L, $MgSO_4$ = 12 mg/L

Find: (a) Temporary hardness (b) Permanent hardness (c) Total hardness in ppm and °F

Solution: (MW: $Ca(HCO_3)_2$ =162, $MgCl_2$ =95, $CaSO_4$ =136, $MgSO_4$ =120)

Salt	mg/L	Formula	$CaCO_3$ equiv
$Ca(HCO_3)_2$	16.2	$\frac{16.2\times100}{162}$	10 ppm (temp)
$MgCl_2$	19.0	$\frac{19\times100}{95}$	20 ppm (perm)
$CaSO_4$	13.6	$\frac{13.6\times100}{136}$	10 ppm (perm)
$MgSO_4$	12.0	$\frac{12\times100}{120}$	10 ppm (perm)
Total			**50 ppm**

Temp. hardness = 10 ppm;

Perm. = 40 ppm; Total = 50 ppm

In °F: 50/10 = **5F**

Lime-Soda Process for Water Softening

Reagents & Reactions

Lime Ca(OH) removes:

- Free CO : $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$
- Temp. Ca^2 : $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$
- Temp. Mg^2 : $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$
- Perm. Mg^2 : $MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$

Soda Na CO removes:

- Perm. Ca^2 : $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$
- Perm. CaSO : $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$

Process:

Cold or hot lime-soda

- **Cold:** 15–30°C; residual hardness 50–80 ppm
- **Hot:** 80–100°C; residual hardness 15–25 ppm

Advantages:

- Cheap reagents
- Large scale treatment
- Removes iron/manganese too

Disadvantages:

- Large sludge disposal
- Not suitable for very high hardness
- Requires skilled operation

Zeolite (Permutit) Process

Principle

Zeolite: Sodium alumino-silicate ($Na\ Al\ Si\ O\ \cdot xH\ O$), represented as $Na\ Ze$

Softening:

$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl$

$Na_2Ze + MgSO_4 \rightarrow MgZe + Na_2SO_4$

Ca^2 /Mg^2 replaced by Na (no hardness)

Regeneration: Exhausted zeolite treated with 10% NaCl brine:

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

Advantages:

- Simple operation, no sludge
- Complete softening possible
- Regeneration is easy (NaCl)
- Compact equipment

Disadvantages:

- Cannot remove turbidity
- Cannot handle acidic water (pH $<$ 6 destroys zeolite)
- Adds Na — not suitable for cardiac patients
- High silica/turbid water clogs zeolite

Synthetic: Dowex, Amberlite — sulfonated polystyrene resin zeolites

Ion Exchange (Deionization) Process

Process

Water passed through two columns:

Column 1 — Cation exchanger (RH):

$R\text{-}H_2 + CaCl_2 \rightarrow R\text{-}Ca + 2HCl$

All cations (Ca^{2}, Mg^{2}, Na) replaced by H

Column 2 — Anion exchanger (R'OH):

$R'\text{-}OH_2 + H_2SO_4 \rightarrow R'\text{-}SO_4 + 2H_2O$

All anions (Cl, SO^{2}, HCO) replaced by OH

$H + OH \rightarrow H\,O \rightarrow$ **demineralized water**

Regeneration:

Cation resin: dilute HCl or H SO

Anion resin: dilute NaOH

Advantages:

- Produces ultra-pure water
- Removes all dissolved salts
- Used in pharmaceutical, electronic, boiler feed

Disadvantages:

- Expensive resins
- Frequent regeneration if high TDS
- Does not remove organics/bacteria

Reverse Osmosis (RO)

Principle

Osmosis: Water moves from low to high solute concentration through semipermeable membrane

RO: Apply pressure $>$ osmotic pressure on saline side $\rightarrow$ water forced through membrane $\rightarrow$ purified water collected

Membrane: Thin-film composite (TFC) — polyamide on polysulfone support; pore size $\sim$0.0001 µm

Operating pressure: Brackish water: 5–20 bar; Seawater: 50–80 bar

What RO removes:

- Dissolved salts (TDS reduction $>$95%)
- Bacteria, viruses
- Heavy metals (Pb, As, Hg)
- Nitrates, fluorides
- Organic compounds

Advantages:

- No chemicals required
- Compact, scalable
- Drinking water, desalination

Disadvantages:

- 30–50% water waste (reject stream)
- Membrane fouling
- Pre-treatment needed

Boiler Feed Water: Requirements & Problems

Requirements

Boiler feed water must be:

- Free from hardness (scale-forming salts)
- Low dissolved O (corrosion prevention)
- Low dissolved CO
- Low TDS (carry-over prevention)
- Neutral to slightly alkaline (pH 8–9)
- Free from suspended solids

Boiler Troubles

Scale/Sludge: Deposition of CaSO , CaCO on boiler walls → poor heat transfer → overheating → explosion risk

Priming: Carrying liquid water droplets with steam (due to dissolved salts/suspended matter → *foamy water*)

Foaming: Stable foam in boiler due to oil, alkali, organic matter

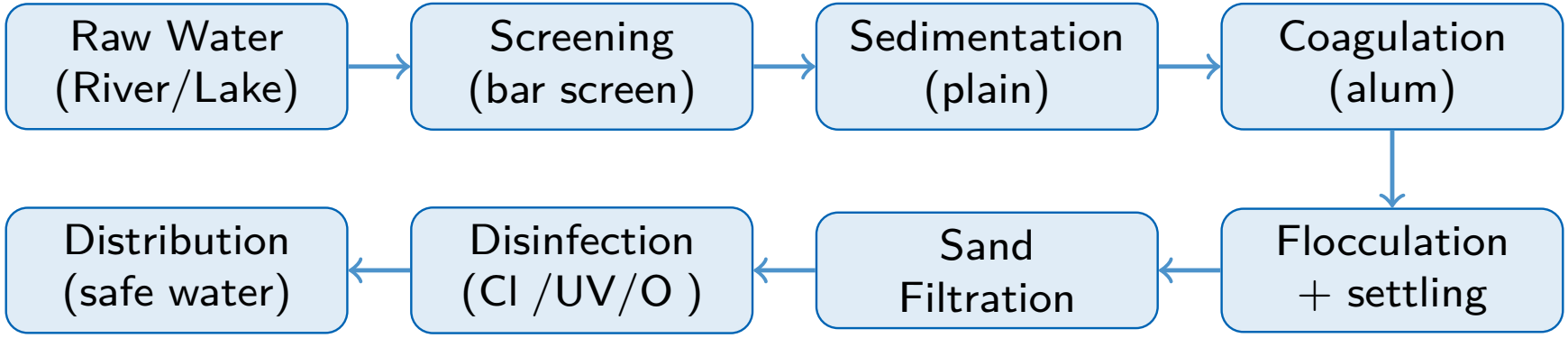
Caustic embrittlement: Leaks near rivets expose metal to NaOH → stress corrosion cracking

Corrosion: Dissolved O , CO attack boiler metal

Prevention of Boiler Troubles

Problem	Cause	Prevention/Treatment
Scale	$CaSO_4$, $CaCO_3$, $Mg(OH)_2$ deposition	Soften feed water; internal conditioning ($NaPO_3$, tannin); blowdown
Sludge	Loose precipitates; $MgCO_3$, $Fe(OH)_3$	Coagulants; frequent blowdown
Priming	High TDS, suspended matter, foamy water	Purify feed water; reduce boiler load; antifoam agents
Foaming	Oil, alkali, dissolved organics	Remove oil; control alkalinity (pH 8–9)
Caustic embrittlement	NaOH concentration in crevices	Add Na_2SO_4 (ratio Na_2SO_4 :NaOH >2.5); rivet welding
O corrosion	Dissolved O_2	Deaeration (heating); add hydrazine (N_2H_4) or sodium sulfite
CO corrosion	Dissolved CO_2 in condensate	Add volatile amines (cyclohexylamine); mechanical deaeration

Municipal Drinking Water Treatment



Key steps explained:

- **Coagulation:** Alum Al (SO) $\rightarrow$ Al(OH) gel adsorbs colloidal particles
- **Disinfection (chlorination):** Cl + H O $\rightarrow$ HOCl + HCl; HOCl kills pathogens; residual Cl maintained 0.2–0.5 mg/L
- **Breakpoint chlorination:** Add Cl until all NH oxidized + free Cl residual appears

Sewage Treatment Process

Primary Treatment

Screening: Bar/fine screens remove large solids

Grit chamber: Sand, grit settle out

Primary sedimentation: Organic suspended solids settle as primary sludge

Removes: 50–65% suspended solids, 30–40% BOD

Secondary Treatment

Biological: Microorganisms decompose dissolved organics

Trickling filter: Sewage sprinkled on stone bed with biofilm

Activated sludge: Sewage + returned activated sludge aerated in tank; bacteria degrade BOD

Secondary clarifier removes biomass
Removes: 85–95% BOD

Tertiary: Nutrient removal (N, P), advanced filtration, disinfection $\rightarrow$ reclaimed water

Desalination of Seawater

Thermal Methods

Multi-Stage Flash (MSF):
Seawater heated $\rightarrow$ flashed through successive chambers at decreasing pressure $\rightarrow$ steam condensed as fresh water
Energy intensive; large scale

Multi-Effect Distillation (MED):
Each effect uses latent heat from previous; more efficient than MSF

Vapour Compression (VC):
Steam compressed $\rightarrow$ condensed $\rightarrow$ heat reused

Membrane Methods

RO (Reverse Osmosis):
Most energy-efficient for seawater (50–80 bar); dominant technology today

Electrodialysis (ED):
Ion-selective membranes; DC voltage drives ions through membranes; best for brackish water ($<$5000 ppm TDS)

Comparison:
RO: 3–4 kWh/m^3 (seawater)
MSF: 10–15 kWh/m^3

Water Softening Methods: Comparison

Feature	Lime-Soda	Zeolite	Ion Exchange
Reagent	Ca(OH) + Na CO	NaCl (regeneration)	HCl/H SO + NaOH
Removes	Ca², Mg², Fe, CO	Ca², Mg² only	All dissolved ions
Residual hardness	15–80 ppm	Nearly zero	Nearly zero (DM water)
Sludge	Yes (large)	No	No
Scale/turbidity	Also removes	Cannot handle	Cannot handle
Adds Na	No	Yes	No
Cost	Low	Moderate	High
Output water	Softened	Softened	Demineralized
Best use	Municipal, industrial	Domestic, industrial	Boiler feed, lab, pharma

Numerical: Lime-Soda Requirement

Worked Example

Problem: A water sample contains:
$Ca(HCO_3)_2 = 32.4$ mg/L $MgSO_4 = 24$ mg/L $MgCl_2 = 19$ mg/L
Find the amount of lime and soda required per litre.

Solution: (MW: $Ca(HCO_3)_2$ =162, $MgSO_4$ =120, $MgCl_2$ =95, $Ca(OH)_2$ =74, Na_2CO_3 =106)

Lime required:
For $Ca(HCO_3)_2$: $\frac{32.4}{162} \times 74 = 14.8$ mg/L
For $MgSO_4$: $\frac{24}{120} \times 74 = 14.8$ mg/L
For $MgCl_2$: $\frac{19}{95} \times 74 = 14.8$ mg/L
Total lime = 44.4 mg/L

Soda required:
For $MgSO_4 \rightarrow$ produces $CaSO_4$: $\frac{24}{120} \times 106 = 21.2$ mg/L
For $MgCl_2 \rightarrow$ produces $CaCl_2$: $\frac{19}{95} \times 106 = 21.2$ mg/L
Total soda = 42.4 mg/L

Boiler Scale: Formation & Harmful Effects

Scale-Forming Salts

Hard scale (difficult to remove):
CaSO ← solubility decreases with temp
CaSiO , MgSiO — very hard

Soft scale (easier to remove):
CaCO , Mg(OH) , MgSiO

$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2$

$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2$

$MgCO_3 + H_2O \rightarrow Mg(OH)_2 \downarrow + CO_2$

Effects of Scale:

- Thermal insulation: scale ($k \approx 0.1$–2 W/mK) vs steel (≈ 50 W/mK) → poor heat transfer
- Overheating of boiler walls → metal weakening
- Risk of explosion
- Increased fuel consumption
- Reduced boiler efficiency and lifespan

Scale Removal:

Mechanical scraping, acid pickling (2% HCl), EDTA chelation treatment

Internal Conditioning of Boiler Water

Problem	Chemical Added	Action
Scale ($CaSO_4$, $CaCO_3$)	Sodium phosphate (Na_3PO_4)	Forms soft, non-adherent $Ca_3(PO_4)_2$ sludge $\rightarrow$ removed by blowdown
Scale (general)	Sodium hexametaphosphate (calgon)	Sequestration — keeps Ca^{2+}/Mg^{2+} in solution as complex
Scale/sludge conditioning	Tannin, lignin	Sludge stays fluid and non-adherent
O_2 corrosion	Hydrazine N_2H_4	$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$; no TDS increase
O_2 corrosion	Sodium sulfite Na_2SO_3	$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$; low pressure boilers only
Caustic embrittlement	Sodium sulfate Na_2SO_4	Ratio Na_2SO_4:NaOH > 2.5 fills crevices
Foaming/priming	Anti-foam agents (castor oil derivatives)	Breaks surface foam

Chlorination: Disinfection of Water

Chemistry of Chlorination

$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$

HOCl (hypochlorous acid) is the active germicide

$HOCl \rightleftharpoons H^+ + OCl^-$

At pH 6–7: HOCl dominant (more effective)
At pH $>$ 8.5: OCl^- dominant (40$\times$ less effective)

Residual Cl : 0.2–0.5 mg/L maintained in distribution network

Breakpoint Chlorination:

As Cl dose increases:
1. Cl reacts with NH $\rightarrow$ chloramines (combined Cl)
2. Chloramines oxidized $\rightarrow$ N at breakpoint
3. Beyond breakpoint: free Cl residual appears

Free Cl is 25$\times$ more effective than combined Cl

Alternatives to Cl :

Ozone (O) — powerful, no by-products, no residual

UV radiation — physical, no chemicals

Chloramine — longer residual, less THM formation

ClO — effective against Cryptosporidium

Water Quality Standards & Water-Borne Diseases

Water-Borne Diseases

Disease	Pathogen
Cholera	Vibrio cholerae
Typhoid	Salmonella typhi
Hepatitis A	HAV virus
Polio	Poliovirus
Dysentery	Shigella / E. coli
Giardiasis	Giardia lamblia
Cryptosporidiosis	Cryptosporidium

BIS/WHO Drinking Water Standards

Parameter	Limit
pH	6.5–8.5
Turbidity	$<$1 NTU
TDS	$<$500 mg/L
Total hardness	$<$200 mg/L
Chloride	$<$250 mg/L
Fluoride	0.6–1.5 mg/L
Nitrate	$<$45 mg/L
Iron	$<$0.3 mg/L
Arsenic	$<$0.01 mg/L
Residual Cl	0.2–0.5 mg/L
Coliform	0 per 100 mL

Sludge Treatment & Disposal

Sludge from Treatment Plants

Primary sludge: Settled raw organics (high BOD)

Secondary sludge: Excess biomass from biological treatment (activated sludge)

Sludge digestion (anaerobic): Methanogens convert organics $\rightarrow$ biogas (60–70% CH_4 + 30% CO_2)

Digested sludge: Stabilized, less odorous; can be used as fertilizer (biosolids)

Sludge Disposal Options:

- **Land application:** Biosolids as agricultural fertilizer (if heavy metal limits met)
- **Landfill:** Dewatered cake disposal
- **Incineration:** High energy; reduces volume 90%
- **Composting:** Combined with wood chips $\rightarrow$ soil amendment

Biogas utilization:

Biogas from sludge digestion powers treatment plant — typical plant can be 50–70% energy self-sufficient

Hardness Numericals: Practice Set

Problems

Q1. Find hardness in ppm if water contains CaCl = 111 mg/L and MgSO = 60 mg/L.
CaCl : $\frac{111\times100}{111} = 100$ *ppm; MgSO :* $\frac{60\times100}{120} = 50$ *ppm; Total =* ***150 ppm***

Q2. Convert 150 ppm hardness to °F and °Cl.
$°F = 150/10 =$ **15F**; $°Cl = 150/14.3 =$ **10.5Cl**

Q3. Water has temporary hardness 50 ppm and permanent 80 ppm. What is total hardness in °F?
Total = 130 ppm; $°F = 130/10 =$ **13F**

Q4. CaSO = 27.2 mg/L in water. Calculate hardness.
MW of CaSO = 136; Hardness = $\frac{27.2\times100}{136} =$ **20 ppm**

Zeolite Process Numerical

Worked Example

Problem: A zeolite softener contains 1000 litres of zeolite with exchange capacity of 5500 litres of water of hardness 100 ppm per cubic metre of zeolite. How many litres of 10% NaCl solution are needed to regenerate it?

Solution:

Volume softened $= 5500$ L per $m^3 \times 1$ $m^3 = 5500$ L

Hardness $= 100$ ppm $= 100$ mg CaCO per litre

Total CaCO equivalent $= 5500 \times 100 = 550{,}000$ mg $= 550$ g

CaCO equivalent moles $= \frac{550}{100} = 5.5$ mol

Reaction: $\mathrm{CaZe} + 2\mathrm{NaCl} \rightarrow \mathrm{Na\ Ze} + \mathrm{CaCl}$

NaCl required $= 2 \times 5.5 = 11$ mol $= 11 \times 58.5 = 643.5$ g

Volume of 10% NaCl $= \frac{643.5}{0.10 \times 1000} = \mathbf{6.435\ L}$

Advanced Water Treatment Technologies

Ultrafiltration (UF):
Membrane pore size 0.01–0.1 µm
Removes bacteria, viruses, colloids
No disinfectant needed

Nanofiltration (NF):
Pore size 0.001–0.01 µm
Removes divalent ions (hardness), organic molecules
Between UF and RO

Ozonation:
O — strong oxidant ($E^\circ = 2.07$ V)
Destroys micropollutants (pesticides, pharmaceuticals)
No chlorine by-products (THMs)

Membrane Spectrum

Process	Pore size	Removes
MF	0.1–10 µm	Suspended soli
UF	0.01–0.1 µm	Bacteria, viruse
NF	1–10 nm	Divalent ions
RO	0.1–1 nm	All dissolved io

Activated Carbon

Removes organic compounds, taste/odour, chlorine from water by adsorption. Surface area 500–1500 m^2/g

Wastewater Reuse & Recycling

Categories of Reuse

Agricultural: Treated wastewater for irrigation (largest reuse globally)

Industrial: Cooling water, process water

Municipal non-potable: Toilet flushing, street cleaning, firefighting

Groundwater recharge: Indirect potable reuse via aquifer

Direct potable reuse: Advanced treated water into drinking supply (emerging)

Zero Liquid Discharge (ZLD):
All wastewater treated and recycled within facility; no effluent discharged

- Mandatory for textile, pharma, tannery in India (CPCB norms)
- Uses evaporators, crystallizers, RO in sequence

Rain Water Harvesting:
Collect roof/surface runoff
Recharge groundwater table

Mandatory in several Indian states for buildings >100 m^2

Water Pollution: Sources & Effects

Source	Pollutants	Effects
Domestic sewage	BOD organics, pathogens, N, P	O depletion, disease, eutrophication
Industrial effluent	Heavy metals, acids, solvents	Toxicity to aquatic life, bioaccumulation
Agricultural runoff	Pesticides, fertilizers (N, P)	Eutrophication, algal blooms, nitrate in groundwater
Thermal power plants	Heated water	Thermal pollution — reduces DO, kills fish
Oil spills	Petroleum hydrocarbons	Coats birds/fish, smothers benthic organisms
Mining	Acid mine drainage ($H\ SO$, Fe^{2})	Acidification, heavy metal contamination
Plastic waste	Microplastics	Accumulate in food chain, hormone disruption

Eutrophication: Excess N, P $\rightarrow$ algal bloom $\rightarrow$ algae die $\rightarrow$ BOD rises $\rightarrow$ DO falls $\rightarrow$ fish kills (dead zone)

Mid-Point Summary: Unit 7

Covered So Far

- ✓ Water quality parameters (physical & chemical)
- ✓ DO, BOD, COD definitions & significance
- ✓ Hardness: types, units, interconversion
- ✓ Hardness numericals (ppm, °F, °Cl)
- ✓ Lime-soda process (all reactions)
- ✓ Zeolite process + regeneration
- ✓ Ion exchange (demineralization)
- ✓ Reverse osmosis + desalination

Still To Come

- PYQ short & 7-mark questions
- More hardness + lime-soda numericals
- Boiler scale numericals
- Fluoride in water (health effects)
- Groundwater contamination
- Exam tips & common errors
- Revision flash points
- Mind map
- Unit summary + course wrap-up

Fluoride in Drinking Water

Fluoride & Health

Optimal: 0.6–1.5 mg/L
Prevents dental caries (tooth decay)

Defluoridation needed when:
>1.5 mg/L (WHO limit)
>1.5 mg/L causes **dental fluorosis** (mottled enamel)
>4 mg/L causes **skeletal fluorosis** (bone deformity)

India context: Fluoride belt in Rajasthan, Gujarat, AP; 20+ states affected

Defluoridation Methods:

- **Nalgonda technique:** Alum + lime → floc adsorbs F ; low cost, widely used in India
- **Activated alumina (AA):** F adsorbed on Al O ; regenerated with NaOH + H SO
- **RO:** Removes >95% fluoride
- **Ion exchange:** Anion resin removes F

Fluoridation: In low-F areas, NaF/H SiF added to reach 1 mg/L

Groundwater Contamination

Major Contaminants

Natural: Arsenic (West Bengal, Bangladesh), Fluoride, Iron, Nitrate from soil

Industrial: Heavy metals (Pb, Cd, Cr, Hg), petroleum hydrocarbons, solvents (TCE, PCE)

Agricultural: Nitrate (NO_3^-), pesticides, herbicides

Urban: Leaking sewers, landfill leachate, road salt

Arsenic in Groundwater:
Reductive mobilisation: FeOOH dissolved under anaerobic conditions releases adsorbed As
India limit: 0.01 mg/L (WHO)

Nitrate Health Effects:
>45 mg/L $\rightarrow$ methemoglobinemia (blue baby syndrome) in infants
$NO_3^- \rightarrow NO_2^-$ binds Hb, reduces O_2 carrying capacity

Remediation:

Pump-and-treat, permeable reactive barriers, phytoremediation, monitored natural attenuation

BOD and COD: Numericals

Worked Examples

Q1. A wastewater sample has initial DO = 9 mg/L. After 5-day incubation at 20°C, DO = 2 mg/L. Find BOD_5.
BOD_5 = Initial DO − Final DO $= 9 - 2 =$ **7 mg/L**

Q2. 0.4 g $K_2Cr_2O_7$ is used to oxidize organics in 250 mL sample. Calculate COD.
MW $K_2Cr_2O_7 = 294$ g/mol; equivalent weight $= 294/6 = 49$

$$\text{Equivalents} = \frac{0.4}{49} = 8.16 \times 10^{-3} \text{ eq}$$

O_2 equivalent wt $= 8$ g/eq

$$\text{COD} = \frac{8.16 \times 10^{-3} \times 8}{0.250} = \mathbf{0.261\ g/L = 261\ mg/L}$$

Q3. BOD/COD ratio = 0.35. Is biodegradation treatment suitable?
Ratio $< 0.4 \rightarrow$ ***not suitable****; industrial/physico-chemical treatment preferred*

PYQ: Short Answer Questions (2 marks) — Set 1

Q. Define hardness of water.

Inability of water to produce lather with soap due to dissolved Ca^{2+} and Mg^{2+} salts of bicarbonates, chlorides and sulphates.

Q. Distinguish temporary and permanent hardness.

Temporary: due to bicarbonates; removed by boiling. Permanent: due to chlorides/sulphates; cannot be removed by boiling.

Q. Define BOD.

Amount of O_2 (mg/L) consumed by microorganisms to biodegrade organic matter at $20^\circ C$ over 5 days. High BOD = highly polluted.

Q. What is scale in boiler? Why harmful?

Hard deposit ($CaSO_4$, $CaCO_3$) on inner boiler walls. Bad heat conductor $\rightarrow$ overheating $\rightarrow$ metal weakening $\rightarrow$ explosion risk + fuel waste.

Q. What is reverse osmosis?

Water forced through semi-permeable membrane under pressure $>$ osmotic pressure. Removes all dissolved ions, bacteria.

Q. What is zeolite process?

Uses $Na_2Al_2Si_2O_8 \cdot xH_2O$ to exchange Na^+ for Ca^{2+}/Mg^{2+}. Regenerated with NaCl.

PYQ: Short Answer Questions (2 marks) — Set 2

Q. What is caustic embrittlement?
Cracking of boiler steel at stressed joints due to concentrated NaOH in crevices. Prevented by adding Na_2SO_4 (ratio $>$ 2.5:1 vs NaOH).

Q. What is priming and foaming?
Priming: carryover of water droplets with steam. Foaming: stable foam on boiler water surface due to dissolved organics/oils.

Q. State principle of ion-exchange softening.
Cation resin (R-H) exchanges H^+ for Ca^{2+}/Mg^{2+}; anion resin (R-OH) exchanges OH^- for Cl^-/SO_4^{2-}. Combined = demineralized water.

Q. What is coagulation and flocculation?
Coagulation: alum $Al_2(SO_4)_3$ hydrolyses to $Al(OH)_3$ gel, neutralizes colloidal charges. Flocculation: gentle stirring aggregates particles into flocs for settling.

Q. Define COD. How does it differ from BOD?
O_2 equivalent of all oxidizable matter (by $K_2Cr_2O_7$). COD $\geq$ BOD always; includes non-biodegradable organics.

Q. What is breakpoint chlorination?
Dose of Cl_2 at which all NH_3 is oxidized to N_2 and free Cl_2 residual begins to appear.

PYQ: 7-Mark — Lime-Soda Process

Explain lime-soda process with all reactions (7 marks)

Principle: Lime [$Ca(OH)_2$] + soda ash [Na_2CO_3] precipitate hardness ions as $CaCO_3$ and $Mg(OH)_2$.

Reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$
$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$
$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaSO_4$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$
$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$

Process: Cold (50–80 ppm residual) or hot ($<$15 ppm). Sludge removed by sedimentation + filtration. Advantages: cheap, removes turbidity, Fe, CO_2. Disadvantage: sludge disposal.

PYQ: 7-Mark — Municipal Drinking Water Treatment

Describe municipal drinking water treatment with flowchart (7 marks)

Screening	Screens remove large debris from river intake
Sedimentation	Plain settling; removes heavy suspended particles
Coagulation	Alum added; $Al(OH)_3$ gel precipitates colloids; pH adjusted with lime
Flocculation	Gentle stirring; flocs grow and settle in clarifier
Sand filtration	Slow or rapid sand filter removes fine particles and bacteria
Disinfection	Cl_2 (0.2–0.5 mg/L residual), ozone, or UV; kills pathogens
pH correction	Lime/CO_2 adjustment to 6.5–8.5
Fluoridation	NaF added if $F^- < 0.6$ mg/L
Distribution	Pumped to overhead tanks and supply network

BIS/WHO limits: pH 6.5–8.5; TDS <500; Hardness <200; Cl_2 residual 0.2 mg/L; Coliform = 0/100 mL

PYQ: 7-Mark — Sewage Treatment

Describe sewage treatment (primary, secondary, tertiary) (7 marks)

Primary (Physical): Screening → Grit chamber → Primary sedimentation tank
Removes 30–40% BOD, 60% SS; produces primary sludge

Secondary (Biological):
Trickling filter: Wastewater trickled over stone/plastic media with biofilm; aerobic oxidation; BOD removal 80–90%
Activated sludge: Aeration tank; microbes consume organics; secondary clarifier; sludge recycled; BOD removal 90–95%

Tertiary: Sand filtration, activated carbon, nutrient removal (N, P), disinfection, RO
Final effluent meets standards for river discharge or reuse

Sludge treatment: Anaerobic digestion → biogas (60–70% CH_4) + biosolids (fertilizer)

CPCB effluent standards: BOD $<$10 mg/L; SS $<$20 mg/L; pH 6.5–9.0

Numerical: Boiler Scale and Zeolite

Worked Examples

Q1. A boiler uses water with hardness 200 ppm. 50,000 litres used per day. Find mass of $CaCO_3$ scale formed.

200 ppm = 200 mg/L

Scale/day $= 200 \times 10^{-3}$ *g/L* $\times$ 50,000 *L* $=$ **10,000 g = 10 kg/day**

Q2. Water contains $CaCl_2$ = 222 mg/L, $MgCl_2$ = 190 mg/L. Zeolite exchange capacity = 85 g $CaCO_3$/kg. Find zeolite needed for 10,000 L.

Hardness ($CaCl_2$): $\frac{222 \times 100}{111}$ = 200 ppm; Hardness ($MgCl_2$): $\frac{190 \times 100}{95}$ = 200 ppm

Total = 400 ppm; $CaCO_3$ equiv $= 400 \times 10^{-3} \times 10{,}000 = 4000$ g

Zeolite $= \frac{4000}{85} \times 1000 =$ **47.06 kg**

Common Exam Errors & Tips

Common Mistakes

- Forgetting $CaCO_3$ equivalent in ppm formula
- Confusing bicarbonates = temporary with chlorides/sulphates = permanent
- Zeolite regenerated by NaCl, not Na_2CO_3
- Mg salts need **two** separate lime-soda reactions
- COD $\geq$ BOD always; never vice versa
- Free CO_2 needs lime in lime-soda process (often forgotten)

Exam Strategy

- Write MW and formula before each numerical step
- Separate each salt in hardness calculations
- Simple flowchart earns diagram marks (5/7-mark Q)
- Memorise all 7 lime-soda reactions
- 2-mark = definition + 1 example = full marks
- Show balanced equations with product states ($\downarrow$, $\uparrow$)
- BOD/COD ratio indicates treatment method choice

Industrial Water: Cooling Systems

Cooling Water Problems

Scale: $CaCO_3$, $CaSO_4$ in heat exchangers

Corrosion: Dissolved O_2, CO_2, microbiological activity

Biofouling: Algae, bacteria (*Legionella* in cooling towers)

Treatments:
Scale inhibitors: polyphosphates, HEDP
Corrosion inhibitors: molybdates, benzotriazole
Biocides: Cl_2, isothiazolone, glutaraldehyde

Cycles of Concentration (CoC):

$$\text{CoC} = \frac{\text{TDS in recirculating water}}{\text{TDS in makeup water}}$$

Higher CoC $\rightarrow$ less makeup water (better efficiency), but higher scaling risk. Typical: 3–5 cycles.

Blowdown: Fraction of recirculating water purged to control TDS buildup.

***Legionella* control:** Residual biocide; periodic hyperchlorination; storage temperatures $>60^\circ$C

Comprehensive Hardness Numerical

Full Classification Example

Problem: Water contains: $Ca(HCO_3)_2 = 16.2$ mg/L; $Mg(HCO_3)_2 = 14.6$ mg/L; $CaSO_4 = 13.6$ mg/L; $MgCl_2 = 9.5$ mg/L. Find temporary, permanent and total hardness in ppm and °F.

Salt	**MW**	**mg/L**	**Hardness (ppm)**
$Ca(HCO_3)_2$	162	16.2	$\frac{16.2\times100}{162} = 10$ (Temp)
$Mg(HCO_3)_2$	146	14.6	$\frac{14.6\times100}{146} = 10$ (Temp)
$CaSO_4$	136	13.6	$\frac{13.6\times100}{136} = 10$ (Perm)
$MgCl_2$	95	9.5	$\frac{9.5\times100}{95} = 10$ (Perm)

Temporary = 10+10 = **20 ppm = 2°F** Permanent = 10+10 = **20 ppm = 2°F**
Total hardness = **40 ppm = 4°F**

Water Conservation & Environmental Regulations

Conservation Strategies

Domestic: Low-flow fixtures, rainwater harvesting, greywater reuse

Agricultural: Drip irrigation (50% less water vs flood), soil moisture monitoring

Industrial: Recirculation cooling, ZLD, water audits

India schemes: Jal Jeevan Mission (piped water to rural households); Atal Bhujal Yojana (groundwater management)

Indian Regulations

Water Act, 1974: Prevention & Control of Pollution

EP Act, 1986: Environment Protection

IS 10500:2012: BIS drinking water standard

CPCB effluent norms:

pH: 6.5–9.0

BOD: $<$30 mg/L (river discharge)

SS: $<$100 mg/L

Oil & grease: $<$10 mg/L

ZLD mandatory: textile, pharma, tannery

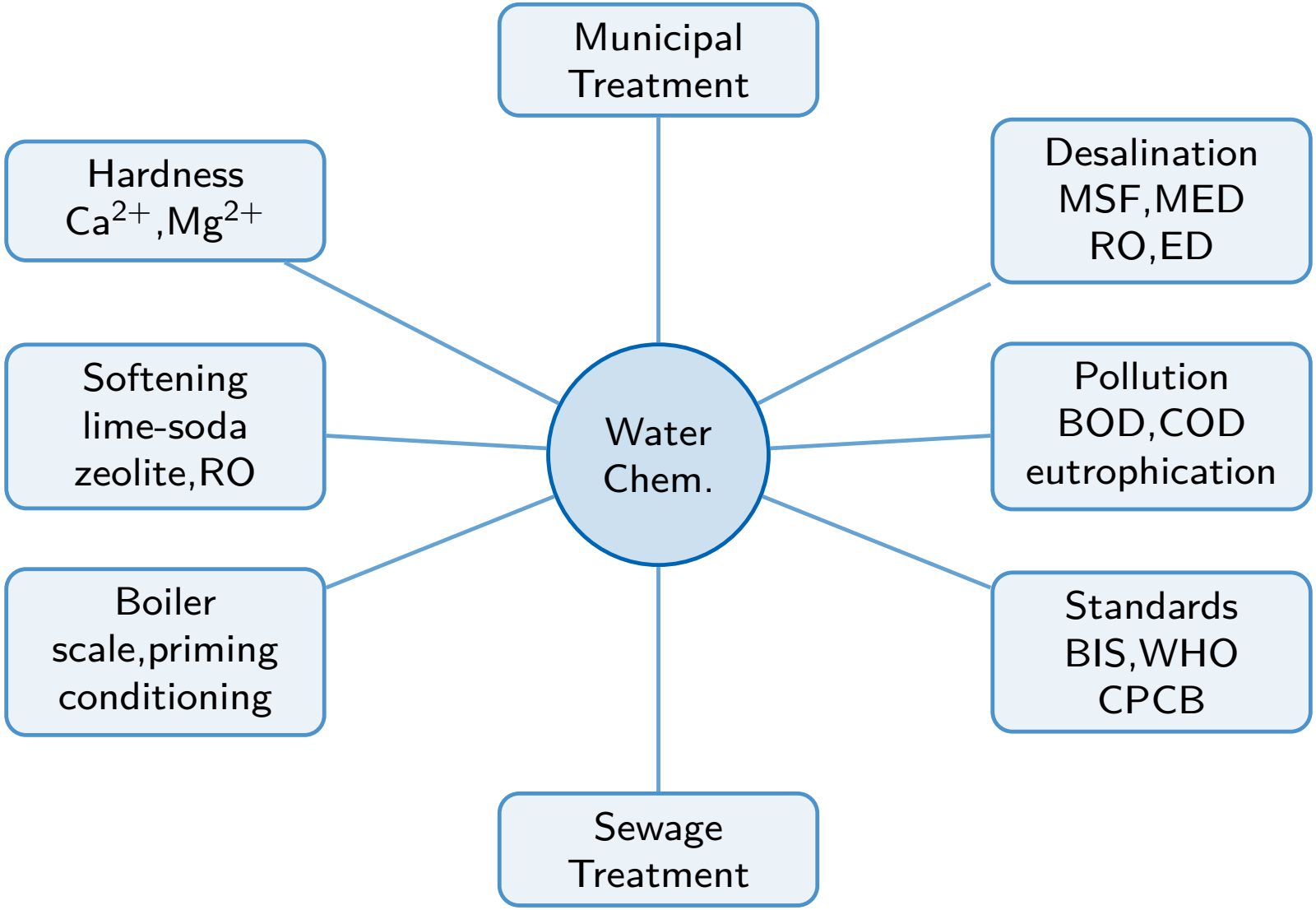
Revision Flash Points: Unit 7

- Hardness ppm = (mg/L $\times$ 100) / MW of salt as $CaCO_3$
- 1 ppm = 0.1°F = 0.07°Cl = 0.056°d
- Temporary hardness = bicarbonate salts; removed by boiling
- Lime-soda: $Ca(OH)_2$ removes temporary; Na_2CO_3 removes permanent Ca; both needed for Mg salts
- Zeolite regenerated by 10% NaCl; cannot remove turbidity
- Ion exchange $\rightarrow$ demineralized (DM) water for boiler feed
- RO: pressure $>$ osmotic pressure; removes all dissolved ions
- Boiler troubles: scale, priming, foaming, caustic embrittlement, corrosion
- Scale: $CaSO_4$ hardest; poor heat transfer $\rightarrow$ explosion risk
- N_2H_4 removes O_2 without adding TDS (high-pressure boilers)
- BOD_5 at 20°C; BOD/COD $< 0.4 \rightarrow$ biological treatment unsuitable
- Breakpoint Cl_2: all NH_3 oxidized; free Cl_2 appears
- BIS: pH 6.5–8.5; TDS <500; hardness <200; F^- 0.6–1.5 mg/L
- Dental fluorosis >1.5 mg/L; skeletal fluorosis >4 mg/L
- Defluoridation: Nalgonda technique or activated alumina
- Sewage: primary (physical) $\rightarrow$ secondary (biological) $\rightarrow$ tertiary
- Anaerobic digestion of sludge $\rightarrow$ biogas (60–70% CH_4)
- Eutrophication: excess N, P $\rightarrow$ algal bloom $\rightarrow$ DO depletion $\rightarrow$ dead zone
- ZLD mandatory for textile/pharma/tannery in India

Key Data & Reactions for Exam

Item	Value / Reaction
Hardness units	1 ppm $= 0.1^\circ$F $= 0.07^\circ$Cl
Hardness formula	$\frac{\text{mg/L} \times 100}{\text{MW}}$ as $CaCO_3$ equivalent
BOD (clean water)	<1 mg/L; polluted river 5–10; sewage 200–500
DO (clean water)	8–9 mg/L; fish survive >4 mg/L
Municipal Cl_2 residual	0.2–0.5 mg/L
Zeolite formula	$Na_2Al_2Si_2O_8 \cdot xH_2O$ (Na_2Ze)
Zeolite regeneration	$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$
Internal conditioning	$3CaSO_4 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 3Na_2SO_4$
O_2 scavenger	$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$
Caustic embrittlement	Na_2SO_4 : NaOH ratio > 2.5
Coagulation	$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 + 6CO_2$

Unit 7: Concept Mind Map



Hardness Numericals: Practice Set

Practice Problems

Q1. Find hardness in ppm: $CaCl_2 = 111$ mg/L; $MgSO_4 = 60$ mg/L.
$CaCl_2$: $\frac{111\times100}{111} = 100$ *ppm;* *$MgSO_4$:* $\frac{60\times100}{120} = 50$ *ppm;* *Total =* ***150 ppm***

Q2. Convert 150 ppm to °F and °Cl.
$^\circ F = 150/10 = \mathbf{15^\circ F}$; $^\circ Cl = 150/14.3 = \mathbf{10.5^\circ Cl}$

Q3. Water: $Ca(HCO_3)_2 = 81$ mg/L; $MgSO_4 = 72$ mg/L; $CaCl_2 = 55.5$ mg/L.
Find temporary and permanent hardness.
Temp: $Ca(HCO_3)_2$ only $= \frac{81\times100}{162} = 50$ *ppm*
Perm: $MgSO_4$: $\frac{72\times100}{120} = 60$; *$CaCl_2$:* $\frac{55.5\times100}{111} = 50$; *Total perm =* ***110 ppm***
Total= ***160 ppm = 16°F***

Numerical: Lime and Soda Required

Lime-Soda Requirement Calculation

Problem: Calculate lime [$Ca(OH)_2$] and soda [Na_2CO_3] required to treat 1 litre of water containing: $Ca(HCO_3)_2 = 32.4$ mg/L; $MgCl_2 = 19$ mg/L; $MgSO_4 = 24$ mg/L.

MW: $Ca(HCO_3)_2$=162; $MgCl_2$=95; $MgSO_4$=120; $Ca(OH)_2$=74; Na_2CO_3=106

Lime required:

For $Ca(HCO_3)_2$: $\frac{32.4}{162} \times 74 = 14.8$ mg/L

For $MgCl_2$ (2 moles lime): $\frac{19}{95} \times 2 \times 74 = 29.6$ mg/L

For $MgSO_4$ (2 moles lime): $\frac{24}{120} \times 2 \times 74 = 29.6$ mg/L

Total lime = 74.0 mg/L

Soda required:

$MgCl_2$ produces $CaCl_2$: $\frac{19}{95} \times 106 = 21.2$ mg/L

$MgSO_4$ produces $CaSO_4$: $\frac{24}{120} \times 106 = 21.2$ mg/L

Total soda = 42.4 mg/L

Key Parameters in Sewage Treatment

Parameter	Typical Sewage	After Treatment
BOD	200–300 mg/L	$<$10 mg/L (tertiary)
COD	300–600 mg/L	$<$50 mg/L
SS	150–300 mg/L	$<$20 mg/L
Total N	30–50 mg/L	$<$10 mg/L
Total P	5–15 mg/L	$<$1 mg/L
pH	7 (neutral)	6.5–9.0
DO	$\approx$0	$>$6 mg/L (after aeration)
Coliforms	10^6–10^9/100 mL	0 (after disinfection)

Treatment Efficiency

Primary: 30–40% BOD removal; Secondary: 85–95% BOD removal; Tertiary: $>$99% BOD removal

RO and Membrane Processes: Summary

Reverse Osmosis in Detail

Osmosis: Solvent flows from dilute to concentrated solution through semi-permeable membrane.

Osmotic pressure: $\Pi = iCRT$ (van't Hoff)

RO: Applied pressure $> \Pi$ forces water through membrane, leaving ions behind.

Seawater $\Pi \approx 27$ bar; operating pressure 50–80 bar
Brackish water: 10–20 bar

Membrane: Thin-film composite (TFC) polyamide; pore $\approx$ 0.1–1 nm
Recovery: 40–85% of feed water recovered

RO Applications:

- Seawater desalination (SWRO)
- Brackish water treatment
- Boiler feed water production
- Industrial pure water
- Pharmaceutical grade water
- Domestic RO systems

R.O. Rejects (brine):
Must be disposed carefully; high TDS brine disposal is an environmental challenge for inland plants.

Pre-treatment for RO:

Coagulation $\rightarrow$ filtration $\rightarrow$ cartridge filter $\rightarrow$ antiscalant dosing $\rightarrow$ RO

Water, Sustainability & Global Perspective

Global Water Facts

Total global water: 1.386 billion km^3
Freshwater: 2.5% only
Accessible freshwater: $<1\%$

2.2 billion people lack safe drinking water (UN, 2022)
4.2 billion lack adequate sanitation

UN SDG 6: Clean water and sanitation for all by 2030

India annual per capita water availability dropping from 5177 m^3 (1951) to $\approx$1486 m^3 (2021)

Indian Water Challenges:

- Groundwater over-extraction (Punjab, Rajasthan, UP)
- River pollution (Ganga, Yamuna)
- Industrial effluents in water bodies
- Arsenic and fluoride in groundwater
- Urban water supply infrastructure gaps

Green Chemistry Approach:

Water-less processes, solvent recycling, minimizing industrial water footprint, eco-friendly effluent treatment technologies

Electrodialysis (ED) & Advanced Desalination

Electrodialysis Principle

DC voltage applied across a stack of alternating cation-exchange membranes (CEM) and anion-exchange membranes (AEM).

Cations move toward cathode through CEM; anions move toward anode through AEM.

Result: dilute and concentrate compartments alternate in stack.

Best for: Brackish water (1000–5000 ppm TDS)
EDR: Electrodialysis Reversal — polarity periodically reversed to prevent fouling

Desalination Technology Comparison

Method	Energy	Best for	Sca
MSF	High	Seawater	Lar
MED	Medium	Seawater	Lar
SWRO	Low	Seawater	All
BWRO	Very low	Brackish	All
ED/EDR	Low	Brackish	Sm me

Water Quality Monitoring & Testing

Laboratory Tests

EDTA titration: Total hardness measurement
$Ca^{2+} + Mg^{2+}$ titrated with 0.01 M EDTA; indicator EBT (wine red $\rightarrow$ blue at endpoint)

Winkler method: DO measurement
$MnSO_4 + KI + H_2SO_4$; I_2 liberated titrated with $Na_2S_2O_3$

Permanganate method: COD (quick estimate)

Dichromate method: Accurate COD

BOD apparatus: DO bottle, 5-day incubation, 20°C dark

Online/Field Monitoring:

- pH meter, conductivity meter, turbidimeter
- DO probe (polarographic or optical)
- TDS meter (conductivity-based)
- Fluoride ISE (ion-selective electrode)
- Spectrophotometer: nitrate, phosphate, chromium
- TOC analyser (Total Organic Carbon)

Real-time monitoring: SCADA systems monitor treatment plant parameters online; alarms for out-of-spec conditions

Microbiological Water Quality

Indicator Organisms

Total Coliforms: Normal inhabitant of gut of warm-blooded animals; indicates fecal contamination risk. Limit: 0/100 mL (drinking water)

E. coli: Specific indicator of fecal contamination; Limit: 0/100 mL

Heterotrophic Plate Count (HPC): General bacterial count; Limit $<$100 CFU/mL

Why coliforms? Easy to detect, survive longer than pathogens, correlate with pathogen presence

Detection Methods

MPN method (Most Probable Number): Multiple tube fermentation; statistical estimate of coliforms per 100 mL

Membrane filtration: 100 mL filtered; incubated on selective media; colonies counted

Rapid methods: Colilert (enzyme substrate), flow cytometry

Presumptive $\rightarrow$ **Confirmed** $\rightarrow$ **Completed** test sequence

PYQ: Short Answer Questions — Set 3

Q. Define dissolved oxygen (DO). What is its significance?

O_2 dissolved in water; determined by Winkler method. Clean natural water: 8–9 mg/L. DO $<$ 4 mg/L: aquatic life stressed. DO $=$ 0: anaerobic (septic) conditions.

Q. What is the significance of BOD/COD ratio?

Ratio indicates biodegradability. $>$0.6: easily biodegradable; 0.4–0.6: biodegradable; $<$0.4: biologically resistant; need chemical/physical treatment.

Q. What is eutrophication?

Excess N and P in water body $\rightarrow$ algal bloom $\rightarrow$ algae die $\rightarrow$ microbial decomposition raises BOD $\rightarrow$ O_2 depletion $\rightarrow$ fish kills (hypoxic/anoxic

Q. What is sedimentation? How is it enhanced?

Settling of suspended particles under gravity. Enhanced by coagulation (alum) and flocculation (gentle stirring) to form larger, faster-settling flocs.

Q. Define TDS. What does high TDS indicate?

Total Dissolved Solids $=$ all dissolved inorganic and organic matter. Measured by evaporation or conductivity. High TDS indicates contamination, industrial effluent, or excessive hardness. Limit: 500 mg/L (BIS).

Q. What is the Nalgonda technique?

Defluoridation: alum $+$ lime added $\rightarrow$ $Al(OH)_3$ floc adsorbs F^- $\rightarrow$ floc settled and filtered. Low-cost, widely used in rural India.

PYQ: 7-Mark — Boiler Troubles & Prevention

Explain boiler troubles and their prevention (7 marks)

Trouble	Cause	Prevention
Scale	$CaSO_4$, $CaCO_3$, $CaSiO_3$ deposits	Na_3PO_4/calgon; blowdown; DM water
Priming	High dissolved/suspended solids; rapid boiling	Slow heating; blowdown; baffle plates
Foaming	Oil, grease, organic matter in water	Remove oils; add anti-foam agents
Caustic embrittlement	NaOH conc. in crevices at stressed joints	Add Na_2SO_4 (ratio >2.5:1); use riveted boilers → welded construction
O_2 corrosion	Dissolved O_2 in feed water	Deaeration + N_2H_4 or Na_2SO_3
CO_2 corrosion	Dissolved CO_2 from bicarbonate decomposition	Add cyclohexylamine or morpholine (neutralising amines)

External treatment: Ion exchange/RO for DM water. **Internal conditioning:** Chemicals added to boiler feed water to control residual impurities.

Complete Hardness Removal Methods: Summary

Method	Removes	Residual	Sludge	Best Use
Boiling	Temporary only	Moderate	$CaCO_3$	Domestic, small scale
Lime-soda (cold)	All types	50–80 ppm	Yes, large	Municipal, industrial
Lime-soda (hot)	All types	$<$15 ppm	Yes	Industrial
Zeolite	All types	$\approx$0	No	Industrial, domestic
Ion exchange (mixed)	All ions	$\approx$0	No	Boiler feed, lab, pharma
RO	All ions	$\approx$0	Brine	Desalination, DM water
Nanofiltration	Divalent ions	Low	Small	Partial softening

Key deciding factors

Scale: Municipal $\rightarrow$ lime-soda; Industrial softening $\rightarrow$ zeolite; Boiler feed (zero hardness required) $\rightarrow$ ion exchange or RO; Desalination $\rightarrow$ SWRO.

Numericals: Osmotic Pressure & Practical Problems

Problems

Q1. Water with 5000 mg/L NaCl. Approximate osmotic pressure? (MW NaCl = 58.5; T = 25°C; $i = 2$)

$C = \frac{5}{58.5} = 0.0855$ mol/L; $\Pi = iCRT = 2 \times 0.0855 \times 0.0831 \times 298 =$ **4.23** bar

Q2. An RO unit has 40% recovery and feed flow 100 L/h. What is product and reject flow?

Product $= 40\% \times 100 = 40$ *L/h;* *Reject (brine)* $=$ **60** *L/h*

Q3. BOD test: 10 mL sample diluted to 300 mL. Initial DO = 9 mg/L; final DO = 3 mg/L. Find BOD.

DO consumed $= 9 - 3 = 6$ mg/L (in 300 mL)

Actual BOD $= 6 \times \frac{300}{10} =$ **180 mg/L**

Unit 7 Exam Strategy & High-Value Topics

Guaranteed 7-Mark Topics

- Lime-soda process (all reactions + advantages)
- Zeolite process (reactions + regeneration)
- Boiler troubles and prevention (full table)
- Municipal drinking water treatment (flowchart)
- Sewage treatment (primary + secondary + tertiary)
- Reverse osmosis (principle + applications)

High-Value Numericals

- Hardness in ppm (all salts given, classify temp/perm)
- Convert ppm to $^\circ$F and $^\circ$Cl
- Lime and soda required for a water sample
- Zeolite volume/NaCl for regeneration
- BOD from DO readings
- Scale formed per day from hardness data

Weightage: $\approx$**15%** of DI01000071 final paper. Expect 1–2 numericals, 2–3 short definitions, and 1 descriptive (process flowchart or boiler troubles).

Engineering Chemistry DI01000071: Complete!

All Units Covered

- ✓ **Unit 1:** Atomic Structure, Bonding & Solutions
- ✓ **Unit 2:** Electrochemistry (EMF, batteries, corrosion)
- ✓ **Unit 3:** Corrosion (types, factors, protection)
- ✓ **Unit 4:** Fuels (classification, calorific values, numericals)
- ✓ **Unit 5:** Lubricants (properties, testing, viscosity)
- ✓ **Unit 6:** Polymers (types, synthesis, properties)
- ✓ **Unit 7:** Water Chemistry (hardness, treatment, boiler)

Exam Preparation Checklist

- ☐ Revise all formulas and key reactions (flashcards)
- ☐ Practice 5+ numericals per unit
- ☐ Draw all process flowcharts from memory
- ☐ Write short definitions for every bold term
- ☐ Attempt 3–4 PYQs without notes
- ☐ Review common errors slide per unit
- ☐ Revise unit mind maps 1 day before exam

Engineering Chemistry

DI01000071

"Water is the driving force of all nature."

— Leonardo da Vinci

Milav Dabgar
Lecturer, Department of Electronics & Communication Engineering
Government Polytechnic Palanpur

All 7 Units Complete ✓