

Swami Ramanand Teerth Marathwada University, Nanded
Faculty of Science & Technology

B.Sc. (CHEMISTRY) FIRST YEAR – SEMESTER I

ORGANIC & INORGANIC CHEMISTRY

Course Code: SCHECT 1101 | Core Major | 2 Credits (Theory)

COMPLETE STUDY NOTES (Syllabus 2026–27)

DEVELOPED FOR OUR STUDENTS

BY
NARSINGH

Unit	Title	Hours
I	An Introduction to Organic Reactions	07
II	Aromatic Hydrocarbons and Aromaticity	05
III	Alcohols, Epoxides and Phenols	08
IV	Periodic Table and Periodicity	10
	Total	30

Total Marks: 50 (Formative 20 + Summative 30)

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Course Objectives and Outcomes

Course Objectives

1. To develop understanding of fundamental concepts in Organic, Inorganic and Physical Chemistry.
2. To enhance analytical, experimental and problem-solving abilities among students.
3. To familiarize students with laboratory techniques, safety procedures and scientific methods.
4. To promote application-oriented, skill-based and research-oriented learning in Chemistry.

Course Outcomes (COs)

CO	Outcome	Bloom's Level	Unit
CO1	Explain basic concepts of organic reactions, reaction intermediates and electronic effects.	Remember / Understand	I
CO2	Interpret aromaticity, electrophilic substitution reactions and orientation effects in aromatic compounds.	Understand / Analyze	II
CO3	Describe preparation, properties and reactions of alcohols, epoxides and phenols.	Apply / Analyze	III
CO4	Explain periodic properties such as ionization energy, electron affinity and electronegativity.	Apply / Evaluate	IV

How to Use these Notes

- Read each unit in the order of the syllabus; the sub-headings follow the numbering 1.1, 1.2 ... of the official syllabus.
- Boxes marked "Quick Revision" summarise each unit for last-minute preparation.
- Practise writing mechanisms stepwise using curved arrows; examiners award marks for each step.
- Practise the Pauling electronegativity numericals at the end of Unit IV.

Recommended Textbooks (from syllabus)

- O.P. Tandon and A.K. Virmani, A New Pattern Text Book of Organic Chemistry for Competition (G.R. Bathla & Sons).
- R.L. Madan, Chemistry for Degree Students (S. Chand).
- Arun Bahl and B.S. Bahl, A Textbook of Organic Chemistry (S. Chand).
- Morrison and Boyd, Organic Chemistry; Peter Sykes, A Guide Book to Mechanism in Organic Chemistry.
- Puri, Sharma and Kalia, Principles of Inorganic Chemistry; J.D. Lee, Concise Inorganic Chemistry.
- E-resources: SWAYAM / NPTEL – Organic Chemistry; SWAYAM – Inorganic Chemistry and Periodicity; e-PG Pathshala.

BEST WISHES !!!!!!!
DR. NARSINGH

UNIT I: An Introduction to Organic Reactions (7 Hours)

1.1 Basic Terms

Substrate

The **substrate** is the organic molecule that is attacked by a reagent and undergoes chemical change. It is usually the larger or more complex molecule in the reaction and supplies the carbon skeleton of the product. For example, in the reaction of methane with chlorine, methane is the substrate; in the nitration of benzene, benzene is the substrate.

Reagent

A **reagent** is the species (atom, ion or molecule) that attacks the substrate and brings about the change. A reagent may be an inorganic or organic compound. On the basis of their behaviour toward electrons, reagents are classified into two broad types: electrophilic and nucleophilic.

Electrophilic reagents (Electrophiles, E^{+})

Electrophiles are electron-loving species. They are electron-deficient and attack centres of high electron density in the substrate. Electrophiles accept an electron pair to form a new covalent bond, so they behave as Lewis acids.

- **Positively charged electrophiles:** H^+ , Cl^+ , Br^+ , NO_2^+ (nitronium), NO^+ , R^+ (carbocations), RCO^+ (acylium), SO_3H^+ .
- **Neutral electrophiles:** these have an atom with an incomplete octet or a vacant orbital, e.g. BF_3 , $AlCl_3$, $FeCl_3$, $ZnCl_2$, SO_3 , carbenes ($:CH_2$), and also carbonyl carbon ($C=O$) and alkyl halides at the carbon bearing the halogen.

Nucleophilic reagents (Nucleophiles, Nu^-)

Nucleophiles are nucleus-loving species. They have a lone pair of electrons or a negative charge and attack centres of low electron density (positive centres) in the substrate. They donate an electron pair, so they behave as Lewis bases.

- **Negatively charged nucleophiles:** OH^- , OR^- , CN^- , Cl^- , Br^- , I^- , NH_2^- , carbanions (R^-), HS^- .
- **Neutral nucleophiles:** species with a lone pair, e.g. H_2O , ROH , NH_3 , RNH_2 , R_2NH , R_3N , ROR , H_2S , and also alkenes and benzene (which donate pi electrons).

Property	Electrophile	Nucleophile
Nature	Electron deficient	Electron rich
Attacks	Electron-rich site	Electron-poor site
Lewis character	Lewis acid (electron pair acceptor)	Lewis base (electron pair donor)
Charge	Positive or neutral with vacant orbital	Negative or neutral with lone pair
Examples	H^+ , NO_2^+ , BF_3 , $AlCl_3$	OH^- , CN^- , NH_3 , H_2O

Note: Nucleophilicity vs. Basicity

Basicity is a thermodynamic property (affinity for a proton) while nucleophilicity is a kinetic property (rate of attack on carbon). Across a period both generally decrease left to right; down a group nucleophilicity increases in protic solvents ($I^- > Br^- > Cl^-$) though basicity decreases.

Notation of Arrows used in Organic Chemistry

Arrows are the language of mechanisms. Each type of arrow has a precise meaning and must be used correctly in answers.

Arrow	Name	Meaning / Use
Curved arrow with full head	Curved (double barbed) arrow	Shows the movement of an electron pair . Tail starts at the source of electrons (a lone pair or bond) and the head points to where the pair ends up. Used in heterolytic mechanisms.
Curved arrow with half head (fish hook)	Half-headed (single barbed) arrow	Shows the movement of a single electron . Used in homolytic (free radical) processes such as bond homolysis and radical chain steps.

Arrow	Name	Meaning / Use
Double-headed straight arrow ($\leftrightarrow$)	Resonance arrow	Placed between resonance contributing structures. It does NOT indicate equilibrium; the real molecule is a hybrid of the structures.
Straight arrow ($\rightarrow$)	Reaction arrow	Shows the direction of a chemical reaction, from reactants to products. Conditions are written over/under it.
Equilibrium arrows ($\rightleftharpoons$)	Equilibrium arrow	Indicates a reversible reaction in which forward and backward reactions occur simultaneously.

Rules for drawing curved arrows: (i) the arrow always starts from the electron-rich site (lone pair or bond) and ends at an electron-poor atom or forms a new bond; (ii) never start an arrow from an atom or a positive charge; (iii) the octet of second-period atoms must not be exceeded; (iv) the total charge must be conserved on both sides.

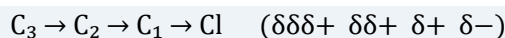
1.2 Electronic Displacement Effects

The distribution of electrons in a covalent molecule is rarely uniform. Because of differences in electronegativity and the presence of pi bonds or lone pairs, electrons are displaced from one atom to another. These displacements explain polarity, acidity, basicity and reactivity. They are classified as **permanent effects** (inductive, resonance/mesomeric, hyperconjugation) and **temporary effects** (electromeric).

A. Inductive Effect (I-effect)

Definition: The permanent displacement of sigma (σ) electrons along a saturated carbon chain due to the presence of an electronegative or electropositive atom or group at one end of the chain is called the inductive effect.

In a C–Cl bond, chlorine is more electronegative than carbon, so the shared pair is pulled toward Cl, giving it a partial negative charge (δ^-) and carbon a partial positive charge (δ^+). This carbon in turn pulls electrons from the next carbon, and so on. The effect decreases rapidly with distance and is practically negligible after the third carbon atom.



The reference standard is hydrogen: groups that attract electrons more strongly than H show a **–I effect**, and groups that release electrons more readily than H show a **+I effect**.

Type	Meaning	Examples (in decreasing order of strength)
–I effect	Electron-withdrawing group	$-\text{NO}_2 > -\text{CN} > -\text{COOH} > -\text{F} > -\text{Cl} > -\text{Br} > -\text{I} > -\text{OH} > -\text{OR} > -\text{C}_6\text{H}_5 > -\text{H}$
+I effect	Electron-releasing group	$(\text{CH}_3)_3\text{C}- > (\text{CH}_3)_2\text{CH}- > \text{CH}_3\text{CH}_2- > \text{CH}_3- > \text{H}$

Characteristics of the inductive effect

- It is a permanent effect operating through sigma bonds.
- It is transmitted only through sigma bonds; electrons are displaced, not transferred completely, so no full charge appears.
- Its magnitude falls steeply with distance (roughly by a factor of about 2.5 per carbon).
- It is a ground state effect and does not require a reagent.

Applications of the inductive effect

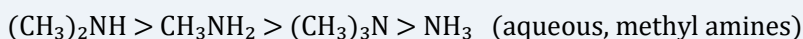
(a) Acidic strength of carboxylic acids. The acidity of an acid depends on the stability of its conjugate base (carboxylate ion). An electron-withdrawing group (–I) disperses the negative charge of the carboxylate ion and stabilises it, increasing acidity. An electron-releasing group (+I) intensifies the negative charge, destabilises the anion and decreases acidity.

Acid	Substituent effect	pK _a (approx.)	Comment
HCOOH	No alkyl group	3.77	Stronger than acetic acid
CH ₃ COOH	+I of CH ₃	4.76	Reference acid
ClCH ₂ COOH	–I of Cl	2.86	Stronger than acetic acid

Acid	Substituent effect	pK _a (approx.)	Comment
Cl ₂ CHCOOH	Two Cl atoms	1.26	Stronger still
Cl ₃ CCOOH	Three Cl atoms	0.65	Strongest in this series
FCH ₂ COOH	–I of F (more than Cl)	2.57	F stronger –I than Cl

Order of acid strength: CCl₃COOH > CHCl₂COOH > CH₂ClCOOH > HCOOH > CH₃COOH > CH₃CH₂COOH. Also, the effect weakens with distance: CH₃CH₂CHClCOOH (2-chlorobutanoic acid) > CH₃CHClCH₂COOH (3-chloro) > ClCH₂CH₂CH₂COOH (4-chloro).

(b) Basic strength of amines. Basicity depends on the availability of the lone pair on nitrogen. +I groups (alkyl) push electron density towards nitrogen and increase basicity, so in the gas phase the order is 3° > 2° > 1° > NH₃. In aqueous solution, solvation (hydrogen bonding stabilisation of the ammonium ion) and steric hindrance modify this order:



Electron-withdrawing groups (–I) such as –Cl or –NO₂ on the alkyl chain reduce basicity, e.g. CH₃NH₂ is a stronger base than ClCH₂NH₂.

Other applications

- Explaining the dipole moment and polarity of molecules such as alkyl halides.
- Explaining reactivity: alkyl halide carbon is electrophilic due to the –I effect of halogens.
- Explaining stability of carbocations (alkyl groups with +I effect stabilise R⁺) and carbanions (alkyl groups destabilise R[–]).

B. Resonance Effect (Mesomeric Effect, M or R effect)

Definition: The permanent polarity produced in a molecule by the interaction (delocalisation) of pi electrons with pi electrons, or pi electrons with lone pairs, in conjugated systems is called the resonance or mesomeric effect.

When a molecule cannot be satisfactorily represented by a single Lewis structure, two or more structures (canonical or contributing structures) that differ only in the position of electrons are written. The actual molecule is a **resonance hybrid** of these structures and is more stable than any one of them. The difference in energy between the most stable contributing structure and the hybrid is called **resonance energy**.

- +R (+M) effect:** the group donates electrons by resonance to the conjugated system. These groups have a lone pair on the atom attached to the system, e.g. –OH, –OR, –NH₂, –NR₂, –X (halogens), –OCOCH₃.
- R (–M) effect:** the group withdraws electrons by resonance from the conjugated system. These groups have a pi bond to an electronegative atom, e.g. –NO₂, –CN, –CHO, >C=O, –COOH, –COOR, –SO₃H.

Example (+R): In aniline the lone pair on nitrogen is delocalised into the ring, placing negative charge at the ortho and para positions. **Example (–R):** In nitrobenzene, ring electrons are drawn toward the nitro group, leaving a positive charge at the ortho and para positions.

Conditions for resonance

- The contributing structures must have the same arrangement of atoms (only electrons move).
- They must have the same number of paired and unpaired electrons.
- The molecule must be planar (or nearly planar) so that p orbitals overlap.
- Structures with a greater number of covalent bonds, complete octets, and minimum charge separation contribute more.

Applications of the resonance effect

(a) Acidic strength. Phenol vs. alcohol: The phenoxide ion is stabilised by delocalisation of the negative charge over the ring (ortho and para positions), whereas the alkoxide ion has no such stabilisation. Hence phenol (pK_a 10) is much more acidic than ethanol (pK_a 16). Carboxylic acids vs. alcohols: the carboxylate ion has two equivalent resonance structures with the charge shared equally on two oxygen atoms, making carboxylic acids (pK_a ~ 4.7) far more acidic than alcohols.

Substituted phenols: An electron-withdrawing group (–NO₂) at ortho or para position further stabilises the phenoxide ion through –R and –I effects, increasing acidity; p-nitrophenol (pK_a 7.15) is more acidic than phenol. An electron-releasing group (–CH₃, –OCH₃) decreases acidity.

(b) Basic strength. Aniline vs. aliphatic amines: the lone pair on nitrogen in aniline is delocalised into the benzene ring and is less available to accept a proton, so aniline (pK_b 9.4) is a much weaker base than cyclohexylamine or methylamine ($pK_b \sim 3.4$). *Amides* are essentially non-basic because the nitrogen lone pair is delocalised toward the carbonyl group. *Guanidine* is a very strong base because its conjugate acid (guanidinium ion) is highly resonance stabilised.

Feature	Inductive effect	Resonance effect
Electrons involved	Sigma electrons	Pi electrons and lone pairs
Distance	Decreases rapidly, felt up to 3 carbons	Operates over the entire conjugated system
Nature	Permanent, partial displacement	Permanent, complete delocalisation
Type of molecule	Saturated and unsaturated	Conjugated systems only
Effect on bond length	Little change	Bond lengths tend to equalise
Planarity requirement	Not required	Required

C. Hyperconjugation (Baker–Nathan Effect)

Definition: The delocalisation of sigma electrons of a C–H bond that is adjacent (alpha) to an unsaturated centre (double bond, triple bond, carbocation or free radical) by overlap with the neighbouring p or pi orbital is called hyperconjugation. It is also called **no-bond resonance** because the structures involve a formal breaking of a C–H bond and the hydrogen carries no bond.

Propene example: The CH_3 group attached to the sp^2 carbon has three alpha C–H bonds. The contributing structures are: $\text{CH}_3\text{--CH=CH}_2 \leftrightarrow \text{H}^+ \text{CH}_2\text{=CH--CH}_2^-$ (and two other equivalent forms, one for each C–H bond). Thus propene has **three** hyperconjugative structures in addition to the normal one.



Effects explained by hyperconjugation

- Stability of alkenes:** the more alkyl groups (more alpha hydrogens) attached to the double bond carbons, the more stable the alkene. Order: $\text{R}_2\text{C=CR}_2 > \text{R}_2\text{C=CHR} > \text{R}_2\text{C=CH}_2 \approx \text{RCH=CHR} > \text{RCH=CH}_2 > \text{CH}_2\text{=CH}_2$. This is Saytzeff (Zaitsev) orientation.
- Stability of carbocations:** tertiary > secondary > primary > methyl, because the number of alpha C–H bonds available for hyperconjugation is 9, 6, 3 and 0 respectively for $(\text{CH}_3)_3\text{C}^+$, $(\text{CH}_3)_2\text{CH}^+$, CH_3CH_2^+ and CH_3^+ .
- Stability of free radicals:** $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ for the same reason.
- Bond length:** hyperconjugation shortens the C–C single bond adjacent to a double bond (partial double bond character) and lengthens the C=C slightly; e.g. in propene the C–C bond (1.50 Å) is shorter than the normal 1.54 Å.
- Dipole moment:** propene (0.36 D) has a larger dipole moment than ethene (zero) as electrons shift from CH_3 toward the double bond.
- Heat of hydrogenation:** more highly substituted alkenes release less heat on hydrogenation as they are more stable.

Exam Tip

Number of hyperconjugative structures = number of alpha hydrogens + 1 (for the normal structure). For tert-butyl cation: 9 alpha H, hence 9 hyperconjugative structures.

Applications in acidic and basic strength (summary)

Compare	Stronger	Reason
Acetic acid vs. formic acid	Formic acid	CH_3 of acetic acid is +I/hyperconjugating and destabilises carboxylate
Phenol vs. ethanol (acidity)	Phenol	Resonance stabilisation of phenoxide ion
p-Nitrophenol vs. phenol	p-Nitrophenol	–R and –I of NO_2 stabilise the phenoxide
Cl_3CCOOH vs. CH_3COOH	Trichloroacetic	Strong –I of three Cl atoms
Methylamine vs. aniline (basicity)	Methylamine	Lone pair of aniline delocalised into ring

Compare	Stronger	Reason
Ethylamine vs. ammonia	Ethylamine	+I effect of ethyl group raises electron density on N
Acetamide vs. ammonia	Ammonia	Amide lone pair delocalised towards C=O

Electromeric effect (brief)

The **electromeric effect (E effect)** is a temporary effect, operating only in the presence of an attacking reagent. A pi bond between two atoms of different electronegativity undergoes complete transfer of the pi pair to one atom on the approach of a reagent. If the transfer is toward the attacking reagent it is a +E effect (e.g. addition of H⁺ to alkenes); if away, -E effect (e.g. addition of CN⁻ to C=O). The effect disappears when the reagent is removed.

1.3 Bond Fission

The breaking of a covalent bond in a molecule is called bond fission (cleavage). Fission may be homolytic or heterolytic depending on how the bonding electron pair is shared between the two atoms.

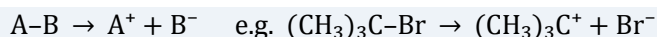
Homolytic fission (Homolysis)

In homolytic fission the bond breaks symmetrically; each atom retains **one electron** of the shared pair and **free radicals** are formed. It is shown by half-headed (fish hook) arrows. It occurs in non-polar bonds, in non-polar solvents or in gas phase, and in presence of heat, UV light or radical initiators such as peroxides.



Heterolytic fission (Heterolysis)

In heterolytic fission the bond breaks unsymmetrically; **both bonding electrons go to the more electronegative atom**, giving a cation and an anion (ionic species). It is shown by a full-headed curved arrow. It occurs in polar bonds, in polar solvents and in presence of acids, bases or catalysts.



Feature	Homolytic fission	Heterolytic fission
Electron distribution	Each fragment gets one electron	Both electrons go to one fragment
Products	Free radicals	Cation and anion (ions)
Arrow used	Half-headed (fish hook)	Full-headed curved arrow
Favoured by	Non-polar medium, heat, light, peroxides	Polar medium, acids/bases, polar bonds
Electronegativity difference	Little or none	Significant
Reaction type	Free radical reactions (chain)	Ionic (polar) reactions

1.4 Types of Organic Reactions

Type	Description	Example
Substitution	An atom or group in the substrate is replaced by another. Can be SN (nucleophilic), SE (electrophilic) or SR (free radical).	$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$
Addition	Two molecules combine to give a single product, mostly at multiple bonds. Can be electrophilic, nucleophilic or radical addition.	$CH_2=CH_2 + Br_2 \rightarrow BrCH_2CH_2Br$
Elimination	Removal of atoms or groups from adjacent carbons to give a multiple bond (E1, E2).	$CH_3CH_2Br + KOH(alc.) \rightarrow CH_2=CH_2 + KBr + H_2O$
Rearrangement	Migration of an atom or group within a molecule leading to an isomer.	$NH_4CNO \rightarrow NH_2CONH_2$ (urea)
Oxidation–reduction	Change in oxidation state / gain of O or loss of H (oxidation), or reverse.	$CH_3CH_2OH \rightarrow CH_3CHO$

Reaction Intermediates

Most organic reactions proceed through unstable, short-lived species formed in one step and consumed in the next. These are called **reaction intermediates**. They are not isolated normally (except in special cases) but their existence is proved by trapping or spectroscopy.

1. Carbocation (Carbonium ion)

A carbocation is a species with a **positively charged carbon** having only six electrons in its valence shell (sextet). It is formed by heterolytic fission when a leaving group departs with the bonding pair.

- **Structure:** the carbon is **sp^2 hybridised**, planar (trigonal planar) with bond angle 120° . The vacant p orbital lies perpendicular to the plane.
- **Formation:** $R-X \rightarrow R^+ + X^-$; protonation of alkenes; protonation of alcohols followed by loss of water.
- **Stability order:** allyl, benzyl $> 3^\circ > 2^\circ > 1^\circ >$ methyl. Stabilised by +I effect, hyperconjugation and resonance (allylic/benzylic).
- **Reactions:** combine with nucleophile; lose a proton to give alkene; rearrange (1,2-hydride or methyl shift) to a more stable carbocation.

2. Carbanion

A carbanion is a species with a **negatively charged carbon** bearing a lone pair (eight electrons, three bond pairs plus one lone pair). It is formed by heterolytic fission in which the electron pair stays with carbon, e.g. by removal of a proton from an acidic C–H by a base.

- **Structure:** carbon is **sp^3 hybridised** and pyramidal like ammonia (when alkyl); when stabilised by resonance (allyl, benzyl, enolate) it is sp^2 and planar.
- **Stability order:** methyl $> 1^\circ > 2^\circ > 3^\circ$ (opposite to carbocations) because +I groups intensify the negative charge. Stabilised by –I, –R groups, and by greater s-character: sp (alkynyl) $> sp^2 > sp^3$.
- **Examples:** Grignard reagent ($R-MgX$ behaves like R^-), acetylide ion, enolate ion, CH_3^- .

3. Free radical

A free radical is a neutral species with an **unpaired electron**, formed by homolytic fission. Carbon radicals have seven electrons in the valence shell.

- **Structure:** alkyl radicals are nearly planar, **sp^2 hybridised** (the unpaired electron is in a p orbital) or rapidly inverting pyramidal; the methyl radical is planar.
- **Stability order:** benzyl, allyl $> 3^\circ > 2^\circ > 1^\circ >$ methyl (hyperconjugation and resonance).
- **Reactions:** chain reactions with initiation, propagation and termination steps, e.g. chlorination of methane; dimerisation (coupling); disproportionation.

4. Carbene

Carbenes are neutral, divalent carbon species of the type $:CR_2$ having **six electrons** in the valence shell (two bonds and a nonbonding pair). The simplest is methylene $:CH_2$.

- **Singlet carbene:** two non-bonding electrons paired in the same sp^2 orbital, with an empty p orbital; bent structure with bond angle $\sim 103^\circ$ for $:CH_2$; shows both nucleophilic and electrophilic character. Stereospecific addition to alkenes.
- **Triplet carbene:** two unpaired electrons in different orbitals (a diradical); more stable for $:CH_2$ in the ground state; linear or nearly linear ($\sim 136^\circ$); adds to alkenes non-stereospecifically.
- **Preparation:** from diazomethane by photolysis or heat ($CH_2N_2 \rightarrow :CH_2 + N_2$); from chloroform with strong base ($CHCl_3 + KOH \rightarrow :CCl_2$) – dichlorocarbene.
- **Reactions:** insertion into C–H bonds, addition to double bonds forming cyclopropanes, and the Reimer–Tiemann reaction.

5. Nitrene (introduction only)

Nitrenes ($R-N:$) are the nitrogen analogues of carbenes: neutral, monovalent nitrogen species with **six electrons** around nitrogen. They are highly reactive and exist as singlet or triplet forms. They are generated from azides on heating or photolysis ($R-N_3 \rightarrow R-N: + N_2$) and are intermediates in the Hofmann, Curtius and Lossen rearrangements.

6. Benzyne (introduction only)

Benzyne (1,2-didehydrobenzene, C_6H_4) is a highly strained, reactive intermediate formed by removal of two ortho substituents from benzene. A "triple bond" is present but the extra pi bond lies in the plane of the ring, formed by sideways overlap of sp^2 orbitals, and is very weak. It is generated from halobenzenes with a strong base ($NaNH_2$) – the elimination–addition mechanism of nucleophilic aromatic substitution – and is trapped by dienes (Diels–Alder).

Intermediate	Hybridisation	Shape	Electrons on central atom	Nature
Carbocation	sp^2	Trigonal planar	6	Electrophile
Carbanion	sp^3	Pyramidal	8	Nucleophile / base
Free radical	sp^2	Planar	7	Neutral, reactive
Carbene (singlet)	sp^2	Bent	6	Ambiphilic
Nitrene	sp	Linear/bent	6	Electrophile
Benzyne	sp^2 (ring)	Planar	–	Highly strained

Stability of carbocations – explanation

For a **tertiary** carbocation like $(CH_3)_3C^+$, three methyl groups donate electron density by the +I effect and nine alpha C–H bonds participate in hyperconjugation, spreading the positive charge widely. For a methyl cation there are no alkyl groups and no hyperconjugation, hence it is least stable. Benzyl and allyl cations enjoy additional resonance stabilisation; e.g. the allyl cation $CH_2=CH-CH_2^+ \leftrightarrow ^+CH_2-CH=CH_2$ delocalises the charge over two carbons.

Quick Revision – Unit I

1. Electrophile = electron-seeking Lewis acid; nucleophile = nucleus-seeking Lewis base.
2. Curved full arrow = pair of electrons; fish hook = single electron.
3. +I/–I are sigma effects; +R/–R are pi effects; hyperconjugation = sigma→pi no-bond resonance.
4. Homolysis → radicals; heterolysis → ions.
5. Carbocation sp^2 planar; carbanion sp^3 pyramidal; radical planar; carbene 6 electrons.

UNIT II: Aromatic Hydrocarbons and Aromaticity (5 Hours)

2.1 Introduction to Aromatic Hydrocarbons

Aromatic hydrocarbons (arenes) are cyclic, planar, conjugated compounds that show unusual stability and characteristic substitution reactions. The term "aromatic" originally referred to the pleasant smell of many natural resins and oils from which these compounds were first obtained, but today it refers to specific structural and electronic features rather than odour. **Benzene** (C_6H_6) is the parent member and was first isolated by Michael Faraday (1825) from compressed illuminating gas.

Aromatic compounds are of two kinds: **benzenoid** (containing one or more benzene rings, e.g. toluene, naphthalene) and **non-benzenoid** (aromatic but without a benzene ring, e.g. tropylium cation, cyclopentadienyl anion, azulene).

Nomenclature of aromatic compounds

Monosubstituted benzenes are named by prefixing the substituent name to "benzene" (e.g. chlorobenzene, nitrobenzene, ethylbenzene). Many have retained common names which are also accepted by IUPAC.

Structure	Common name	IUPAC name
$C_6H_5-CH_3$	Toluene	Methylbenzene
C_6H_5-OH	Phenol	Benzenol (phenol retained)
$C_6H_5-NH_2$	Aniline	Benzenamine
C_6H_5-COOH	Benzoic acid	Benzenecarboxylic acid
C_6H_5-CHO	Benzaldehyde	Benzenecarbaldehyde
$C_6H_5-CH=CH_2$	Styrene	Ethenylbenzene
$C_6H_5-OCH_3$	Anisole	Methoxybenzene
$C_6H_5-SO_3H$	Benzenesulphonic acid	Benzenesulfonic acid
$C_6H_5-COCH_3$	Acetophenone	1-Phenylethanone

Disubstituted benzenes have three isomers, designated by locants 1,2 (ortho, o-), 1,3 (meta, m-) and 1,4 (para, p-). Examples: o-xylene (1,2-dimethylbenzene), m-dichlorobenzene (1,3-dichlorobenzene), p-nitrotoluene (1-methyl-4-nitrobenzene). When there are three or more substituents, numbers are used and the lowest set of locants is chosen, with substituents cited alphabetically. The C_6H_5- group is called **phenyl** and the $C_6H_5CH_2-$ group is **benzyl**.

Structure of Benzene

Molecular formula and evidence

Benzene has the molecular formula C_6H_6 , indicating a high degree of unsaturation (four degrees: DBE = 4). Yet it does not behave like an alkene: it does not decolourise bromine water or Baeyer's reagent readily and undergoes substitution rather than addition. Key facts: (i) all six carbons and six hydrogens are equivalent – only one monosubstituted product exists; (ii) only **three** disubstituted isomers exist; (iii) all C–C bond lengths are equal (139 pm), intermediate between a single (154 pm) and a double bond (134 pm); (iv) the molecule is planar with bond angles of 120° .

Kekulé structure (1865)

Kekulé proposed a planar cyclic hexagon of six carbons with alternating single and double bonds, each carbon carrying one hydrogen. To explain why only one ortho-disubstituted isomer (1,2-) exists, he suggested that benzene exists as two rapidly interconverting structures (oscillating double bonds).

Kekulé structure I $\rightleftharpoons$ Kekulé structure II (double bonds shift position)

Limitations of the Kekulé structure: It cannot explain the unusual stability of benzene (resistance to addition), the equal C–C bond lengths, or why benzene gives substitution rather than addition reactions. The heat of hydrogenation of the hypothetical cyclohexatriene would be three times that of cyclohexene ($3 \times 120 = 360$ kJ/mol) but the observed value for benzene is only 208 kJ/mol – meaning benzene is more stable by about **152 kJ/mol** (the resonance or stabilisation energy).

Resonance structure of benzene

According to the resonance theory, benzene is a hybrid of two equivalent Kekulé structures (I and II) and three less-contributing Dewar structures. The two Kekulé structures differ only in the positions of the pi electrons. The true structure is intermediate (a resonance hybrid), is more stable than any contributing structure, and the C–C bonds are all identical with bond order 1.5. Delocalisation of six pi electrons over the entire ring is represented by a circle inside the hexagon.

- Resonance energy of benzene $\approx 150\text{--}152$ kJ/mol (36 kcal/mol).
- The double-headed arrow ($\longleftrightarrow$) is used between resonance structures – not equilibrium arrows.
- Dewar structures (bridged bicyclic) contribute very little because they involve long bonds and strain.

Orbital picture of benzene

The modern orbital (molecular orbital / valence bond) picture describes benzene as follows:

1. Each of the six carbon atoms is **sp^2 hybridised**. Of the three sp^2 orbitals, two overlap with sp^2 orbitals of neighbouring carbons (forming C–C sigma bonds) and one overlaps with the 1s orbital of hydrogen (C–H sigma bond).
2. This gives a planar hexagonal sigma framework with all bond angles of **120°** .
3. Each carbon has one unhybridised **p orbital** perpendicular to the plane of the ring, containing one electron.
4. The six p orbitals overlap sideways (laterally) with both neighbours, forming a continuous **delocalised pi electron cloud** above and below the plane of the ring – a "doughnut" of electron density.
5. The six pi electrons are delocalised over all six carbon atoms, so all C–C bonds are equivalent (139 pm).

In molecular orbital terms, six p orbitals combine to form six pi molecular orbitals: three bonding (ψ_1, ψ_2, ψ_3) and three antibonding ($\psi_4^*, \psi_5^*, \psi_6^*$). ψ_1 is the lowest (all in phase); ψ_2 and ψ_3 are degenerate. The six electrons fill the three bonding orbitals completely, giving a closed-shell, highly stable configuration, and this is the origin of aromatic stability.

Stability of benzene

- Resonance (delocalisation) energy of about 152 kJ/mol.
- Complete filling of all bonding molecular orbitals with six pi electrons (closed shell).
- Planarity permits maximum overlap of p orbitals.
- Reactions that keep the aromatic sextet intact (substitution) are preferred over addition, which would destroy the aromatic stabilisation.

2.2 Aromaticity, Antiaromaticity and Homoaromaticity

Hückel's rule ($4n + 2$ rule)

Erich Hückel (1931) stated that a planar, cyclic, fully conjugated molecule containing **$(4n + 2)$ pi electrons** (where $n = 0, 1, 2, 3 \dots$), i.e. 2, 6, 10, 14, 18 ... pi electrons, is **aromatic**, and shows exceptional stability.

Conditions for aromaticity

1. The molecule must be **cyclic**.
2. It must be **planar** (all atoms in the ring sp^2 or p-hybridised, allowing p-orbital overlap).
3. The ring must have a **continuous cyclic conjugation** of p orbitals (no sp^3 atom interrupting the ring).
4. The number of pi electrons must satisfy Hückel's rule: **$4n + 2$** .

Aromatic, antiaromatic and non-aromatic

Class	Criteria	Number of π electrons	Stability	Examples
Aromatic	Cyclic, planar, conjugated	$4n + 2$ (2, 6, 10 ...)	Extra stable	Benzene, naphthalene, pyridine, cyclopentadienyl anion, tropylium cation
Antiaromatic	Cyclic, planar, conjugated	$4n$ (4, 8, 12 ...)	Highly unstable	Cyclobutadiene, cyclopentadienyl cation, cyclooctatetraene (if planar)
Non-aromatic	Not cyclic or not planar or not fully conjugated	Any	Normal	Cyclohexene, cyclooctatetraene (tub-shaped), cyclopentadiene

Examples of aromatic systems

- **Benzene:** 6 π electrons ($n = 1$). Aromatic.
- **Naphthalene:** 10 π electrons ($n = 2$). Aromatic. **Anthracene:** 14 π electrons ($n = 3$).
- **Cyclopropenyl cation ($C_3H_3^+$):** 2 π electrons ($n = 0$). Aromatic.
- **Cyclopentadienyl anion ($C_5H_5^-$):** 6 π electrons. Aromatic. Cyclopentadiene ($pK_a \sim 16$) is unusually acidic for a hydrocarbon because the conjugate base is aromatic.
- **Tropylium (cycloheptatrienyl) cation ($C_7H_7^+$):** 6 π electrons. Aromatic and a stable carbocation (isolable as tropylium bromide).
- **Cyclobutadiene:** 4 π electrons ($n = 1$ in $4n$). Antiaromatic, extremely reactive and dimerises even at very low temperature.
- **Cyclooctatetraene:** 8 π electrons; adopts a non-planar tub shape to avoid antiaromaticity, so it is non-aromatic and behaves like a polyene.

Heterocyclic aromatic compounds

Heterocyclic compounds have one or more heteroatoms (N, O, S) in the ring. They are aromatic when the lone pair or pi electrons give a total of $4n + 2$ electrons in the planar conjugated ring.

Compound	Hetero atom	Electrons contributed	Total π electrons	Aromatic?
Pyridine	N (sp^2), lone pair in plane of ring	1 (from N=C), lone pair NOT in ring π system	6	Yes
Pyrrole	N-H, lone pair in p orbital	2 from N lone pair + 4 from two C=C	6	Yes
Furan	O, one lone pair in p orbital	2 from O + 4 from two C=C	6	Yes
Thiophene	S, one lone pair in p orbital	2 from S + 4 from two C=C	6	Yes
Pyrimidine	Two N	Each N contributes 1	6	Yes
Imidazole	Two N (one pyrrole-type, one pyridine-type)	2 (pyrrole-type N lone pair) + 2 (C=C) + 2 (C=N)	6	Yes

Pyridine vs. pyrrole: in pyridine the nitrogen lone pair lies in the plane of the ring (in an sp^2 orbital) and is available for protonation, so pyridine is basic (pK_b 8.8). In pyrrole the lone pair is part of the aromatic sextet and is not available, so pyrrole is a very weak base (the pyrrolic N-H is even weakly acidic).

Antiaromaticity

Antiaromatic compounds are cyclic, planar, fully conjugated species with **$4n \pi$ electrons**. The delocalisation raises the energy (destabilisation) relative to an open-chain analogue. Cyclobutadiene is rectangular (alternating single/double bonds) rather than square to reduce the destabilisation. Molecules avoid antiaromaticity by puckering (cyclooctatetraene) or distortion.

Homoaromaticity

Homoaromatic compounds are systems in which the cyclic conjugation is interrupted by a single sp^3 carbon (a "homo" or extra CH_2 group) but the pi orbitals still overlap through space across this sp^3 centre, giving aromatic-like stability. The classic example is the **homotropylium cation ($C_8H_9^+$)**, formed by protonating cyclooctatetraene in strong acid. It has 6 π electrons delocalised over seven carbon atoms, the eighth carbon being the sp^3 CH_2 with one H pointing into the ring and the other outside. Other examples: cyclopropylcarbinyl-type cations and the trishomocyclopropenyl cation.

Memory Aid

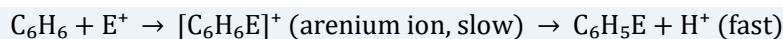
Aromatic = $4n+2$ (stable); Antiaromatic = $4n$ (unstable); Homoaromatic = through-space conjugation across one sp^3 carbon. Always check planarity first!

2.3 Electrophilic Aromatic Substitution (EAS) of Benzene

The pi cloud of benzene is a source of electrons and makes the ring nucleophilic, but because of the resonance stabilisation it prefers to retain aromaticity. Therefore, with electrophiles, benzene undergoes **substitution** (H replaced by E) instead of addition.

General mechanism

1. **Generation of the electrophile (E^+):** by reaction of the reagent with a catalyst (Lewis acid or protic acid).
2. **Attack on the ring (slow, rate determining step):** the pi electrons of benzene attack E^+ , forming a resonance-stabilised, non-aromatic carbocation called the **arenium ion (sigma complex or Wheland intermediate)**. The positive charge is delocalised over the ortho and para carbons.
3. **Loss of proton (fast):** a base removes H^+ from the sp^3 carbon bearing both H and E; the electron pair returns to the ring, regenerating aromaticity.



Evidence: absence of kinetic isotope effect ($k_H/k_D \approx 1$) shows that C–H bond breaking is not the rate-determining step; the arenium ion has been isolated in some cases at low temperatures.

(a) Nitration

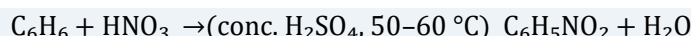
Reagent: a mixture of concentrated nitric acid and concentrated sulphuric acid ("nitrating mixture") at 50–60 °C.

Step 1 – Generation of nitronium ion (NO_2^+): sulphuric acid, the stronger acid, protonates nitric acid, which loses water.



Step 2 – Attack: the pi electrons of benzene attack NO_2^+ , forming the arenium ion (sigma complex) in the slow step.

Step 3 – Deprotonation: HSO_4^- (or H_2O) removes the proton from the sp^3 carbon, restoring the aromatic ring to give nitrobenzene.



At higher temperature (~100 °C) with fuming HNO_3 further nitration gives m-dinitrobenzene, because the nitro group deactivates the ring.

(b) Halogenation

Reagent: Cl_2 or Br_2 in the presence of a Lewis acid catalyst such as anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ (in the dark).

1. **Generation of electrophile:** the Lewis acid polarises the halogen molecule: $Br-Br + FeBr_3 \rightarrow Br^{\delta+} \cdots Br-FeBr_3^{\delta-}$ (effectively $Br^+ + FeBr_4^-$).
2. **Attack:** benzene pi electrons attack the electrophilic bromine atom, forming the arenium ion and $FeBr_4^-$.
3. **Deprotonation:** $FeBr_4^-$ removes the proton giving bromobenzene, HBr and regenerating the $FeBr_3$ catalyst.



Iodination needs an oxidising agent (HNO_3) to remove HI, and fluorination is too violent to control. In the absence of catalyst but in sunlight, chlorine adds to benzene to form benzene hexachloride (BHC, gammexane) by a free radical addition.

(c) Friedel–Crafts Alkylation

Reaction: benzene reacts with an alkyl halide in the presence of anhydrous $AlCl_3$ to give an alkylbenzene.

1. **Generation of carbocation:** $CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$ (polarised complex, effectively a carbocation).
2. **Attack:** benzene attacks the carbocation giving the arenium ion.
3. **Deprotonation:** $AlCl_4^-$ removes H^+ , giving toluene, HCl and regenerating $AlCl_3$.



Limitations of Friedel–Crafts alkylation

- **Polyalkylation:** the product (alkylbenzene) is more reactive than benzene (alkyl is activating), so more than one alkyl group enters. Excess benzene is used to minimise it.
- **Carbocation rearrangement:** primary carbocations rearrange to more stable ones (1,2-hydride shift). n-Propyl chloride gives isopropylbenzene (cumene) as the main product, not n-propylbenzene.
- **Deactivated rings do not react:** benzene bearing strongly deactivating groups ($-NO_2$, $-CN$, $-COR$, $-SO_3H$) fail to react. Also amino groups ($-NH_2$) coordinate with $AlCl_3$.

- **Aryl and vinyl halides** cannot be used, as their carbocations are too unstable.
- The reaction is reversible.

(d) Friedel–Crafts Acylation

Reaction: benzene reacts with an acid chloride (RCOCl) or an acid anhydride in the presence of anhydrous AlCl_3 to give an aryl ketone.

1. **Generation of acylium ion:** $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{C}\equiv\text{O}^+$ (acylium ion, resonance stabilised) + AlCl_4^- .
2. **Attack:** the pi electrons of benzene attack the acylium ion forming the arenium ion.
3. **Deprotonation:** AlCl_4^- removes H^+ , giving acetophenone. The product ketone forms a complex with AlCl_3 , so slightly more than one equivalent of AlCl_3 is used.



Feature	F–C Alkylation	F–C Acylation
Reagent	$\text{R-X} + \text{AlCl}_3$	RCOCl or $(\text{RCO})_2\text{O} + \text{AlCl}_3$
Electrophile	Carbocation (R^+)	Acylium ion (RCO^+)
Rearrangement	Occurs	Does not occur
Polysubstitution	Common (product more reactive)	Absent (product deactivated)
Catalyst amount	Catalytic	Stoichiometric or more
Product	Alkylbenzene	Aryl ketone (reducible to alkylbenzene by Clemmensen)

Synthetic note: To prepare n-propylbenzene avoiding rearrangement, benzene is acylated with propanoyl chloride and the resulting ketone is reduced by Clemmensen reduction (Zn-Hg/HCl) or Wolff–Kishner reduction.

2.4 Orientation Effect of Substituents

When a monosubstituted benzene ($\text{C}_6\text{H}_5\text{-G}$) undergoes a second electrophilic substitution, the incoming group is directed to a specific position (ortho, meta or para) determined by the group G already present. G also changes the **rate** of reaction relative to benzene. Thus every substituent has two effects: **orienting (directing)** and **activating/deactivating**.

Classification of substituents

Class	Effect on rate	Directing	Examples
Strongly activating	Much faster than benzene	o, p	$-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{OH}$, $-\text{O}^-$
Moderately activating	Faster	o, p	$-\text{OR}$, $-\text{NHCOCH}_3$, $-\text{OCOR}$
Weakly activating	Slightly faster	o, p	$-\text{CH}_3$, $-\text{C}_2\text{H}_5$, other alkyl, $-\text{C}_6\text{H}_5$
Weakly deactivating	Slower	o, p	$-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$
Moderately deactivating	Slower	meta	$-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CN}$, $-\text{SO}_3\text{H}$
Strongly deactivating	Much slower	meta	$-\text{NO}_2$, $-\text{NR}_3^+$, $-\text{CF}_3$, $-\text{CCl}_3$

General rule: all activating groups are ortho–para directors; all deactivating groups are meta directors **except halogens**, which deactivate but direct ortho–para.

Explanation based on the stability of the arenium ion

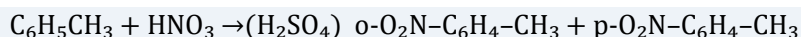
Attack of E^+ at ortho, meta or para position gives three different arenium ions. The directing effect is decided by which intermediate is most stabilised by group G.

Activating groups: $-\text{OH}$, $-\text{CH}_3$ (ortho–para directing)

Phenol ($-\text{OH}$, $+\text{R} > -\text{I}$): Attack at ortho or para positions gives arenium ions in which one of the resonance structures places the positive charge on the carbon bearing the $-\text{OH}$ group. This structure is specially stable because oxygen can donate a lone pair to give an oxonium-type ion in which every atom has a complete octet. No such extra structure exists for meta

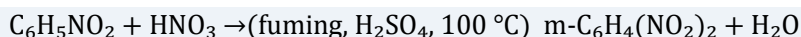
attack. Thus ortho/para intermediates are lower in energy, and the reaction is faster than with benzene. Nitration of phenol occurs even with dilute HNO_3 at room temperature giving o- and p-nitrophenol.

Toluene ($-\text{CH}_3$), +I and hyperconjugation): Ortho or para attack gives an arenium ion with a **tertiary carbocation** contributor (positive charge on the carbon bearing CH_3), stabilised by the +I effect and hyperconjugation. Meta attack never places the charge on that carbon and is less stabilised. Hence nitration of toluene gives o-nitrotoluene (~58%), p-nitrotoluene (~38%) and only a little m-nitrotoluene (~4%).



Deactivating group: $-\text{NO}_2$ (meta directing)

The nitro group is strongly electron-withdrawing by both $-I$ and $-R$ effects. For ortho or para attack, one of the resonance structures of the arenium ion places the positive charge on the carbon directly bonded to the $-\text{NO}_2$ group; this is extremely unfavourable because two adjacent positive charges (partial) are destabilising. In meta attack, this arrangement never occurs, so the meta intermediate is the least destabilised. Thus the incoming electrophile goes **meta**, although the overall reaction is much slower than for benzene. Nitration of nitrobenzene needs fuming HNO_3 /conc. H_2SO_4 at ~100 °C to give m-dinitrobenzene (~93%).



Halogen ($-\text{Cl}$): deactivating but ortho–para directing

Chlorine is strongly electronegative and withdraws electrons through the sigma framework ($-I$ effect), which makes the ring less electron-rich than benzene and therefore **deactivates** it. However, chlorine has lone pairs that can be donated through resonance ($+R$ effect), which stabilises the arenium ions from ortho and para attack (a structure in which Cl^+ carries the charge with a full octet). The inductive effect controls the **rate** (deactivation) while the resonance effect controls the **orientation** (o,p). Nitration of chlorobenzene gives mainly p-chloronitrobenzene (~70%) and o-chloronitrobenzene (~30%), at a slower rate than benzene.



Substituent	Electronic effect	Rate vs benzene	Orientation	Major nitration products
$-\text{OH}$	$+R > -I$	Faster (activating)	o, p	o- and p-nitrophenol
$-\text{CH}_3$	$+I$, hyperconjugation	Faster (activating)	o, p	o- and p-nitrotoluene
$-\text{Cl}$	$-I > +R$	Slower (deactivating)	o, p	p- (major) and o-chloronitrobenzene
$-\text{NO}_2$	$-I$ and $-R$	Much slower	meta	m-dinitrobenzene

Quick Revision – Unit II

1. Benzene: sp^2 carbons, planar, 120° , bond length 139 pm, resonance energy ~152 kJ/mol.
2. Hückel: planar, cyclic, conjugated, $(4n+2)$ π electrons = aromatic; $4n$ = antiaromatic.
3. EAS: E^+ generation $\rightarrow$ arenium ion (slow) $\rightarrow$ loss of H^+ (fast).
4. Nitration: NO_2^+ ; Halogenation: X^+ with FeX_3 ; F–C alkylation: R^+ ; acylation: RCO^+ (AlCl_3).
5. Activating groups ($-\text{OH}$, $-\text{CH}_3$) are o,p; deactivating ($-\text{NO}_2$) are meta; halogens deactivate but are o,p.

UNIT III: Alcohols, Epoxides and Phenols (8 Hours)

3.1 Alcohols: Introduction, Nomenclature and Classification

Alcohols are organic compounds in which one or more hydroxyl (-OH) groups are attached to a **saturated sp^3 carbon** atom. The general formula of a monohydric alcohol is $\text{C}_n\text{H}_{2n+1}\text{OH}$ (R-OH). The functional group is the hydroxyl group; the C-O-H bond angle is about 109° and the oxygen is sp^3 hybridised.

Nomenclature

Common system: the name of the alkyl group followed by the word "alcohol", e.g. methyl alcohol, ethyl alcohol, isopropyl alcohol, tert-butyl alcohol.

IUPAC system: The longest carbon chain containing the -OH group is selected; the final "e" of the alkane name is replaced by "ol"; the chain is numbered to give the -OH group the lowest locant. For diols "diol" and for triols "triol" is used (retaining the "e" of the alkane).

Structure	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	n-Propyl alcohol	Propan-1-ol
$(\text{CH}_3)_2\text{CHOH}$	Isopropyl alcohol	Propan-2-ol
$(\text{CH}_3)_3\text{COH}$	tert-Butyl alcohol	2-Methylpropan-2-ol
$\text{CH}_2\text{OH-CH}_2\text{OH}$	Ethylene glycol	Ethane-1,2-diol
$\text{CH}_2\text{OH-CHOH-CH}_2\text{OH}$	Glycerol (glycerine)	Propane-1,2,3-triol
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	Benzyl alcohol	Phenylmethanol

Classification of alcohols

(i) On the basis of number of hydroxyl groups:

- **Monohydric:** one -OH group, e.g. $\text{CH}_3\text{CH}_2\text{OH}$.
- **Dihydric (glycols):** two -OH groups, e.g. ethylene glycol.
- **Trihydric:** three -OH groups, e.g. glycerol.
- **Polyhydric:** more than three -OH groups, e.g. sorbitol, mannitol.

(ii) On the basis of the carbon bearing the -OH group (monohydric alcohols):

Class	Carbon bearing OH	Example
Primary (1°)	Attached to one (or no) other carbon	$\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH
Secondary (2°)	Attached to two other carbons	$(\text{CH}_3)_2\text{CHOH}$
Tertiary (3°)	Attached to three other carbons	$(\text{CH}_3)_3\text{COH}$

(iii) Other classes: allylic alcohols (OH on carbon next to $\text{C}=\text{C}$), benzylic alcohols (OH on carbon next to benzene ring), and vinylic alcohols (enols, OH on a sp^2 carbon of $\text{C}=\text{C}$ – unstable and tautomerise to carbonyl compounds).

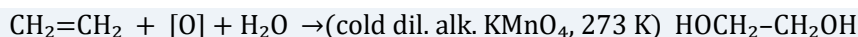
Physical properties (brief): Lower alcohols are colourless liquids with high boiling points compared with alkanes, ethers and haloalkanes of similar molar mass, because of **intermolecular hydrogen bonding**. Solubility in water falls as the alkyl chain lengthens (methanol, ethanol, propanol are miscible; solubility is minimal from C_6 upwards). Boiling points: primary > secondary > tertiary (isomers) due to decreasing surface area.

3.2 Dihydric Alcohol: Ethylene Glycol (Ethane-1,2-diol)

Ethylene glycol, $\text{HOCH}_2\text{-CH}_2\text{OH}$, is the simplest dihydric alcohol (a vicinal diol or 1,2-glycol). It is a colourless, viscous, sweet-tasting, poisonous liquid (b.p. 197°C), miscible with water. It is widely used as an **antifreeze** in car radiators, in the manufacture of polyester (terylene/PET) and as a solvent.

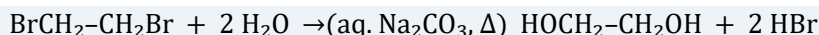
Preparation methods

(i) Hydroxylation of alkene (ethene). Ethene is oxidised with cold, dilute, alkaline potassium permanganate (Baeyer's reagent) to give ethylene glycol by syn addition of two –OH groups across the double bond. The purple colour of KMnO_4 disappears (test for unsaturation). Alternatively, peroxy acids followed by hydrolysis or OsO_4 can be used.



Mechanism (outline): A cyclic manganate ester forms through concerted addition of MnO_4^- to the double bond (syn addition); hydrolysis of the cyclic ester then gives the diol and MnO_2 .

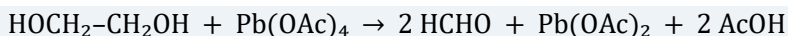
(ii) From 1,2-dihaloalkane (ethylene dibromide or dichloride). 1,2-Dibromoethane is hydrolysed by heating with aqueous sodium carbonate (or aqueous KOH/NaOH) to give ethylene glycol. Aqueous sodium carbonate is preferred because strong alkali would give elimination to alkenes/alkynes.



Industrial method: Ethene $\rightarrow$ ethylene oxide (air, Ag catalyst, 250°C) $\rightarrow$ hydrolysis (water, 200°C , 1.5 MPa) gives ethylene glycol.

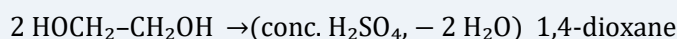
Chemical reactions

1. Oxidative cleavage with lead tetra-acetate, $\text{Pb}(\text{OAc})_4$ (Criegee oxidation). Ethylene glycol, being a vicinal diol, undergoes cleavage of the C–C bond with $\text{Pb}(\text{OAc})_4$ (in glacial acetic acid or benzene) to form **two molecules of formaldehyde (methanal)**. The reaction proceeds through a cyclic lead(IV) ester intermediate that fragments with the formation of C=O bonds; $\text{Pb}(\text{IV})$ is reduced to $\text{Pb}(\text{OAc})_2$.



Periodic acid (HIO_4 , Malaprade reaction) does the same on vicinal diols in aqueous medium. Both reagents are used to prove the presence of vicinal diol groups and in structural determination of sugars.

2. Dehydration with P_2O_5 or ZnCl_2 . Ethylene glycol, when heated with dehydrating agents like P_2O_5 or anhydrous ZnCl_2 , loses water. The product depends on conditions: with ZnCl_2 or P_2O_5 , loss of one molecule of water gives **vinyl alcohol (enol)** which tautomerises to **acetaldehyde**; intermolecular dehydration (with conc. H_2SO_4 or at higher temperature) gives **1,4-dioxane** (a cyclic diether, an excellent solvent).



Other important reactions of ethylene glycol

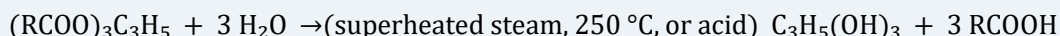
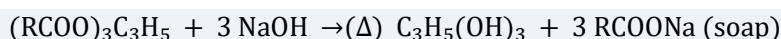
- **With sodium:** forms mono- and disodium glycolate with evolution of H_2 .
- **With HCl/PCl_5 :** gives ethylene chlorohydrin (2-chloroethanol) and then 1,2-dichloroethane.
- **With acids:** forms mono and diesters; with terephthalic acid forms polyester (PET, Terylene).
- **Oxidation:** with HNO_3 gives a mixture of glycolic acid, glyoxal, glyoxylic acid and oxalic acid, depending on the oxidant.
- **With conc. $\text{HNO}_3/\text{H}_2\text{SO}_4$:** gives glycol dinitrate (explosive).

3.3 Trihydric Alcohol: Glycerol (Propane-1,2,3-triol)

Glycerol (glycerine), $\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$, is the most important trihydric alcohol. It is a colourless, odourless, viscous, hygroscopic, sweet-tasting liquid (b.p. 290°C with decomposition), miscible with water and ethanol. It is obtained as a by-product of soap manufacture. The high boiling point and viscosity are due to extensive hydrogen bonding.

Preparation methods

(i) From oils and fats (saponification / hydrolysis). Natural oils and fats are triglycerides, i.e. triesters of glycerol with long-chain fatty acids. Hydrolysis with superheated steam, dilute acid or alkali (NaOH) liberates glycerol.



In the soap industry the aqueous layer (spent lye) contains glycerol; it is neutralised, evaporated and purified by vacuum distillation.

(ii) From propene (synthetic route). Propene is chlorinated at high temperature (500°C) by free radical substitution at the allylic position to give allyl chloride. Reaction with hypochlorous acid (HOCl) gives dichlorohydrins, which on hydrolysis with aqueous NaOH (or Na_2CO_3) give glycerol.



An alternative is the epichlorohydrin route: allyl chloride $\rightarrow$ epichlorohydrin $\rightarrow$ hydrolysis $\rightarrow$ glycerol.

Chemical reactions

1. Action of nitric acid. With a mixture of concentrated nitric acid and concentrated sulphuric acid (the sulphuric acid acts as a dehydrating agent) at low temperature (below 10 °C), all three hydroxyl groups are esterified, giving **glyceryl trinitrate (nitroglycerine)**, a pale yellow, oily and highly explosive liquid. It is mixed with kieselguhr to produce dynamite (Nobel, 1867). In dilute form it is used in medicine as a vasodilator for angina.



With oxalic acid at 110 °C, glycerol gives formic acid; at 260 °C allyl alcohol. With dilute HNO_3 , oxidation gives glyceric acid.

2. Action of acetyl chloride. Glycerol reacts with acetyl chloride (acetylation) to replace the hydrogen atoms of $-\text{OH}$ groups by acetyl groups. Depending on the quantity of acetyl chloride, mono-, di- or **triacetin (glyceryl triacetate)** is formed with evolution of HCl .



Other reactions of glycerol

- **Dehydration with KHSO_4 or P_2O_5 :** gives acrolein (propenal, $\text{CH}_2=\text{CH}-\text{CHO}$), an irritant, pungent smelling compound; this is the test for glycerol and fats (acrolein test).
- **With HI :** forms allyl iodide and then isopropyl iodide.
- **With PCl_5 :** gives 1,2,3-trichloropropane.
- **With sodium:** forms sodium glycerolates with release of hydrogen.
- **Oxidation:** with mild oxidants gives glyceraldehyde/dihydroxyacetone; with strong oxidants gives tartronic and mesoxalic acids.
- **With HNO_3 (dilute):** glyceric acid and tartronic acid.

Uses of glycerol

- Manufacture of explosives (nitroglycerine, dynamite), and of glyptal resins (with phthalic anhydride).
- Cosmetics, soaps, toothpastes, lotions (humectant), pharmaceuticals and syrups.
- Printing inks, lubricants, antifreeze mixtures and food preservation.

Property	Ethylene glycol	Glycerol
Formula	$\text{HOCH}_2\text{CH}_2\text{OH}$	$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$
No. of OH groups	2 (vicinal)	3 (two 1°, one 2°)
b.p.	197 °C	290 °C (dec.)
Reaction with $\text{Pb}(\text{OAc})_4$	2 HCHO	$\text{HCHO} + \text{HCOOH} + \dots$ (cleaves both C–C bonds)
Major use	Antifreeze, polyester	Nitroglycerine, cosmetics, pharma

3.4 Epoxides

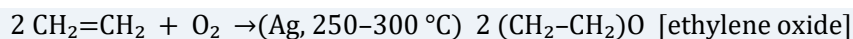
Epoxides (oxiranes, 1,2-epoxides) are cyclic ethers containing a **three-membered ring** made of one oxygen and two carbon atoms. The simplest epoxide is ethylene oxide (oxirane). The bond angles in the ring are about 60°, far from the normal tetrahedral angle (109.5°), so the ring is highly **strained** (angle strain, ~114 kJ/mol). This strain makes epoxides much more reactive than ordinary ethers, and they readily undergo ring-opening reactions with a wide range of nucleophiles.

Nomenclature

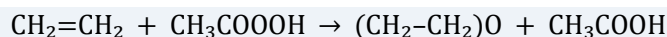
- **IUPAC (as oxirane):** the ring is numbered with oxygen as position 1. $\text{CH}_2-\text{CH}_2(\text{O})$ is **oxirane**; the methyl-substituted compound (propylene oxide) is **2-methyloxirane**.
- **Epoxy prefix:** as substituent, "epoxy" is used, e.g. 1,2-epoxypropane.
- **Common name:** named as "alkene oxide": ethylene oxide, propylene oxide, styrene oxide.

Preparation of epoxides

(a) Oxidation of ethene in the presence of silver catalyst (industrial). Ethene mixed with air or oxygen is passed over silver catalyst at 250–300 °C and 10–20 atm pressure to give ethylene oxide. This is the commercial method; ethylene oxide is a key raw material for ethylene glycol, surfactants and polymers.



(b) Epoxidation of ethene with peracetic acid (peroxy acid). Alkenes react with peroxycarboxylic acids such as peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$), perbenzoic acid, or m-CPBA in a single concerted step (Prilezhaev reaction). The peracid transfers an oxygen atom to the double bond by syn addition (the "butterfly mechanism"); the acid is regenerated as a by-product. The stereochemistry of the alkene is retained (cis-alkene gives cis-epoxide).



(c) Via halohydrin (laboratory method). Alkene + $\text{Br}_2/\text{H}_2\text{O}$ gives bromohydrin; treatment with base (NaOH) brings about intramolecular Williamson-type $\text{S}_\text{N}2$ ring closure to give the epoxide.

Properties

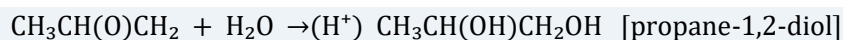
Ethylene oxide is a colourless, toxic, flammable gas (b.p. 10.7 °C), soluble in water, which polymerises in presence of acid or base catalysts to give polyethylene glycol (PEG).

3.5 Chemical Reactions of Epoxides (Ring-opening of Propylene Oxide)

The strain relief that accompanies ring opening is the driving force. Ring opening occurs by nucleophilic attack on one of the epoxide carbons with cleavage of a C–O bond ($\text{S}_\text{N}2$ -like). The regiochemistry in an unsymmetrical epoxide such as **propylene oxide (2-methyloxirane)** depends on whether the conditions are acidic or basic.

(a) Hydrolysis in acidic medium

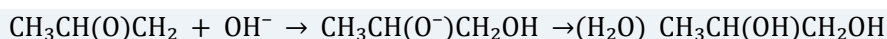
Mechanism: (1) The epoxide oxygen is protonated by H_3O^+ , making it a better leaving group and creating partial positive character on carbons. (2) Water attacks as a nucleophile at the **more substituted carbon** (secondary carbon), which can better stabilise the developing positive charge ($\text{S}_\text{N}1$ -like character); the C–O bond cleaves from the backside (inversion). (3) Loss of proton gives the diol.



The result is trans (anti) addition of the two hydroxyl groups in cyclic epoxides.

(b) Hydrolysis in basic medium

Mechanism: The strong nucleophile OH^- attacks directly at the **less hindered (less substituted) carbon** (primary carbon, CH_2) in a pure $\text{S}_\text{N}2$ manner, opening the ring to form an alkoxide ion, which is protonated by water to give the diol. Steric factors control the position of attack.



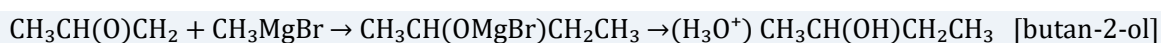
Note: both acid and base hydrolysis give the same product (propane-1,2-diol) when water/hydroxide is the nucleophile. The difference becomes clear with other nucleophiles (e.g. alcohols or HX), where acid catalysis gives attack at C-2 and base catalysis at C-1.

(c) Action of Grignard reagent

Grignard reagents (RMgX) are strong carbon nucleophiles and bases. They attack the **less hindered carbon** of the epoxide in an $\text{S}_\text{N}2$ fashion, causing ring opening to give a magnesium alkoxide, which on acidic workup (dilute HCl or aq. NH_4Cl) gives an alcohol. With ethylene oxide the product is a **primary alcohol having two more carbon atoms** than the Grignard reagent (a useful chain-lengthening method).



For propylene oxide with methylmagnesium bromide, attack occurs at the CH_2 carbon, producing after hydrolysis **butan-2-ol** (a secondary alcohol):



Condition	Nucleophile	Site of attack on propylene oxide	Product (with H_2O)
Acidic	H_2O (weak Nu)	More substituted carbon (C-2) – $\text{S}_\text{N}1$ -like	Propane-1,2-diol
Basic	OH^- (strong Nu)	Less hindered carbon (C-1) – $\text{S}_\text{N}2$	Propane-1,2-diol

Condition	Nucleophile	Site of attack on propylene oxide	Product (with H ₂ O)
Grignard	RMgX (strong Nu)	Less hindered carbon (C-1)	Secondary alcohol, CH ₃ CH(OH)CH ₂ R

Other reactions of ethylene oxide

- With NH₃: gives mono-, di- and triethanolamines.
- With HCl: gives ethylene chlorohydrin; with alcohols gives cellosolves (2-alkoxyethanols).
- With water: ethylene glycol; with excess ethylene oxide: diethylene glycol and polyethylene glycols.
- With HCN: ethylene cyanohydrin.

3.6 Phenols

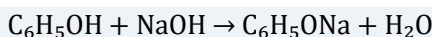
Phenols are organic compounds in which one or more hydroxyl groups are directly attached to a carbon of a **benzene ring (sp² carbon)**. The simplest member is phenol, C₆H₅OH (carbolic acid), obtained from coal tar. Phenols differ from alcohols in being more acidic and in giving ring substitution easily.

Classification of phenols

- **Monohydric**: one OH group – phenol and cresols (o-, m-, p-methylphenol), naphthols.
- **Dihydric**: two OH groups – catechol (1,2-), resorcinol (1,3-), quinol or hydroquinone (1,4-benzenediol).
- **Trihydric**: three OH groups – pyrogallol (1,2,3), phloroglucinol (1,3,5).

Acidic character of phenol (compared with ethanol)

Phenol is a weak acid (pK_a = 10.0) but much stronger than ethanol (pK_a = 15.9) and water (15.7). It reacts with NaOH to form sodium phenoxide but, unlike carboxylic acids, does not liberate CO₂ from NaHCO₃ (phenol is weaker than carbonic acid).



Reason: The acid strength depends on the stability of the conjugate base. In **phenoxide** ion, the negative charge on oxygen is delocalised into the benzene ring through resonance (charge appears at ortho and para carbons) so it is stabilised. In **ethoxide** (C₂H₅O⁻), the +I effect of the ethyl group pushes electrons toward oxygen, intensifying the negative charge and destabilising the ion; no delocalisation occurs. Also, in phenol the oxygen is attached to an sp² carbon (more electronegative than sp³), which withdraws electrons and facilitates loss of H⁺.

Feature	Phenol	Ethanol
Carbon bearing OH	sp ² (aromatic)	sp ³ (aliphatic)
Conjugate base	Phenoxide – resonance stabilised	Ethoxide – destabilised by +I
pK _a	~10	~16
Reaction with NaOH	Yes	No
Reaction with FeCl ₃	Violet colour	No colour
Ring substitution	Very easy	Not applicable

Effect of substituents: electron-withdrawing groups at o/p positions (–NO₂, –Cl, –CN) increase acidity (2,4,6-trinitrophenol or picric acid, pK_a 0.4, is as strong as a mineral acid); electron-donating groups (–CH₃, –OCH₃) decrease acidity (p-cresol pK_a 10.2).

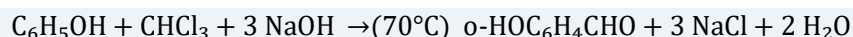
Preparation of phenol (brief)

- **Cumene process (industrial):** cumene is oxidised by air to cumene hydroperoxide, which is cleaved with dilute H₂SO₄ to phenol and acetone.
- **From benzenesulphonic acid:** fusion with NaOH followed by acidification.
- **From diazonium salt:** benzenediazonium chloride is warmed with water.
- **Dow process:** chlorobenzene is heated with NaOH at 350 °C and 300 atm.

Chemical Reactions of Phenol with Mechanism

1. Reimer–Tiemann reaction

Phenol, when heated with **chloroform and aqueous sodium hydroxide** followed by acidification, gives **salicylaldehyde (2-hydroxybenzaldehyde)** as the major product, along with a little p-hydroxybenzaldehyde. This is an ortho-formylation reaction.



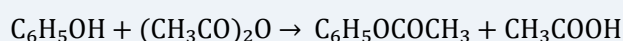
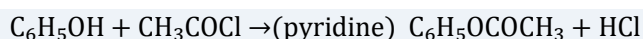
Mechanism:

1. **Formation of dichlorocarbene:** NaOH removes a proton from chloroform to give the trichloromethyl carbanion ($:\text{CCl}_3^-$), which loses Cl^- (alpha-elimination) forming the electrophilic **dichlorocarbene ($:\text{CCl}_2$)**.
2. **Formation of phenoxide:** NaOH deprotonates phenol, giving the phenoxide ion, whose ring is highly activated (negative charge at ortho and para positions).
3. **Electrophilic attack:** the electron-rich ortho carbon of phenoxide attacks the electron-deficient dichlorocarbene, forming a dichloromethyl-substituted intermediate (after tautomerisation, restoration of aromaticity).
4. **Hydrolysis:** the $-\text{CHCl}_2$ group is hydrolysed by aqueous alkali (replacing the Cl atoms by OH, giving an unstable gem-diol that loses water) to produce the aldehyde group ($-\text{CHO}$). Acidification gives salicylaldehyde.

With CCl_4 in place of CHCl_3 , the product is salicylic acid (Reimer–Tiemann carboxylation).

2. Acetylation

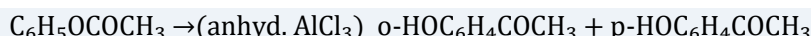
Acetylation is the introduction of an acetyl group ($\text{CH}_3\text{CO}-$) in place of the hydrogen of the phenolic $-\text{OH}$ group. Phenol reacts with acetyl chloride or acetic anhydride (usually in presence of a base such as pyridine or a trace of H_2SO_4) to give **phenyl acetate**.



Mechanism (nucleophilic acyl substitution): The lone pair of phenolic oxygen (or phenoxide) attacks the carbonyl carbon of the acylating agent, forming a tetrahedral intermediate; collapse of this intermediate expels the leaving group (Cl^- or CH_3COO^-), and loss of H^+ gives the ester. Aspirin is made by acetylation of salicylic acid. Acetylation protects the $-\text{OH}$ group.

3. Fries rearrangement

When a **phenolic ester** (e.g. phenyl acetate) is heated with anhydrous aluminium chloride (Lewis acid), the acyl group migrates from the oxygen to the aromatic ring, giving a mixture of **o- and p-hydroxyacetophenones** (hydroxyaryl ketones). It is an intermolecular, electrophilic rearrangement.



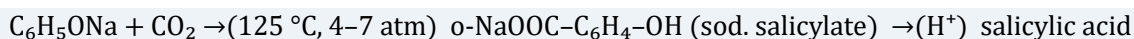
Mechanism:

1. AlCl_3 coordinates to the carbonyl oxygen of the ester (the more electron-rich site).
2. The complex undergoes cleavage of the O–acyl bond giving an acylium ion ($\text{CH}_3\text{C}\equiv\text{O}^+$) and an aluminium phenoxide species ($\text{AlCl}_3\text{--O--C}_6\text{H}_5$).
3. The acylium ion attacks the activated ring (at the o- or p- position of the phenoxide) in an electrophilic aromatic substitution, as in Friedel–Crafts acylation.
4. Loss of proton and hydrolysis (work-up) gives o/p-hydroxyacetophenone.

Temperature control: at low temperature (below 60°C) the para isomer is favoured (kinetic control); at high temperature (above 160°C) the ortho isomer predominates because it forms a stable chelate with AlCl_3 (intramolecular hydrogen bonded chelate). Non-polar solvents also favour the ortho product.

4. Kolbe's carboxylation reaction (Kolbe–Schmitt reaction)

Sodium phenoxide, when heated with **carbon dioxide under pressure (4–7 atm) at 125°C** , followed by acidification with dilute HCl or H_2SO_4 , yields **salicylic acid (2-hydroxybenzoic acid)**. This is used industrially to make salicylic acid, the precursor of aspirin.



Mechanism:

1. Phenol is converted into sodium phenoxide with NaOH; the phenoxide ring is strongly activated at ortho and para positions.

- Carbon dioxide, a weak electrophile (the carbon of CO_2 is electron-deficient), is attacked by the ortho carbon of phenoxide ion, which carries high electron density. A keto-type (cyclohexadienone) intermediate forms.
- Tautomerisation (proton shift) restores aromaticity, giving sodium salicylate.
- Acidification liberates salicylic acid.

The use of sodium phenoxide gives ortho product (via a chelated complex with Na^+); with potassium phenoxide at higher temperature the para isomer (p-hydroxybenzoic acid) forms.

Other reactions of phenol

- Nitration:** dilute HNO_3 gives o- and p-nitrophenol; conc. HNO_3 gives 2,4,6-trinitrophenol (picric acid).
- Bromination:** bromine water gives 2,4,6-tribromophenol, a white precipitate (test for phenol).
- Ferric chloride test:** neutral FeCl_3 gives violet/blue-violet colouration.
- Liebermann's nitroso test; Phthalein reaction:** phenol with phthalic anhydride and conc. H_2SO_4 gives phenolphthalein.
- Reaction with zinc dust:** distillation reduces phenol to benzene.
- Williamson ether synthesis:** sodium phenoxide with alkyl halide gives alkyl aryl ether (anisole with CH_3I).
- Hydrogenation:** with H_2/Ni at 150°C gives cyclohexanol.

Reaction	Reagents	Product	Key intermediate
Reimer–Tiemann	CHCl_3 , NaOH , then H^+	Salicylaldehyde	Dichlorocarbene
Acetylation	CH_3COCl or $(\text{CH}_3\text{CO})_2\text{O}$	Phenyl acetate	Tetrahedral intermediate
Fries rearrangement	Phenyl acetate, AlCl_3 , Δ	o/p-Hydroxyacetophenone	Acylium ion
Kolbe's carboxylation	$\text{C}_6\text{H}_5\text{ONa}$, CO_2 , 125°C , 4–7 atm, then H^+	Salicylic acid	Phenoxide attacks CO_2

Quick Revision – Unit III

- Ethylene glycol: $\text{Pb}(\text{OAc})_4 \rightarrow 2 \text{HCHO}$; $\text{P}_2\text{O}_5/\text{ZnCl}_2 \rightarrow \text{CH}_3\text{CHO}$ (via enol).
- Glycerol: $\text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow$ nitroglycerine; $\text{CH}_3\text{COCl} \rightarrow$ triacetin; $\text{KHSO}_4 \rightarrow$ acrolein.
- Epoxides: made by Ag/O_2 or peracid; ring opens easily because of angle strain.
- Acidic ring opening $\rightarrow$ attack at more substituted C; basic/Grignard $\rightarrow$ attack at less hindered C.
- Phenol is more acidic than ethanol due to resonance-stabilised phenoxide.
- Reimer–Tiemann ($:\text{CCl}_2$), Fries (acylium), Kolbe (CO_2) all involve electrophilic attack on activated ring.

UNIT IV: Periodic Table and Periodicity (10 Hours)

4.1 Development of the Periodic Table

Brief history

Scientist	Year	Contribution
Johann Döbereiner	1817–1829	Law of Triads: in a triad of similar elements the atomic mass of the middle element is the mean of the other two (Li, Na, K; Ca, Sr, Ba; Cl, Br, I).
John Newlands	1864	Law of Octaves: every eighth element has properties similar to the first when arranged by atomic mass. Failed beyond calcium.
Lothar Meyer	1869	Plotted atomic volume against atomic mass; periodic curve showing recurring properties.
Dmitri Mendeleev	1869	Periodic Law: properties of elements are a periodic function of their atomic masses. Left gaps for undiscovered elements (eka-aluminium = gallium, eka-silicon = germanium) and corrected atomic masses.
Henry Moseley	1913	X-ray studies showed that atomic number (not mass) is the fundamental property: $\sqrt{v} = a(Z - b)$.
Modern form	20th century	Modern periodic law based on atomic number; long form (Bohr's form) of the periodic table.

Defects of Mendeleev's table: hydrogen had no fixed place; isotopes had no place; some elements with higher atomic mass were placed before those with lower mass (Ar–K, Co–Ni, Te–I); similar and dissimilar elements were grouped together; lanthanoids and actinoids had no proper position.

Modern periodic law

Statement: "The physical and chemical properties of the elements are a periodic function of their atomic numbers." When elements are arranged in the increasing order of atomic number, elements with similar properties recur at regular intervals.

Long form of the periodic table

The modern table has **7 horizontal rows (periods)** and **18 vertical columns (groups)**, per IUPAC numbering 1 to 18. Periods correspond to the principal quantum number n of the outermost shell.

Period	Name	Number of elements	Orbitals being filled
1	Shortest	2 (H, He)	1s
2	Short	8 (Li–Ne)	2s, 2p
3	Short	8 (Na–Ar)	3s, 3p
4	Long	18 (K–Kr)	4s, 3d, 4p
5	Long	18 (Rb–Xe)	5s, 4d, 5p
6	Longest	32 (Cs–Rn)	6s, 4f, 5d, 6p
7	Incomplete	Up to 118 (Fr–Og)	7s, 5f, 6d, 7p

Cause of periodicity

The periodic repetition of properties is due to the **periodic recurrence of similar outer (valence) shell electronic configurations** after certain regular intervals of atomic number. For example, all alkali metals have ns^1 configuration, and all halogens ns^2np^5 ; hence they have similar chemical behaviour.

Division into blocks: s, p, d and f

Block	Groups	General configuration	General characteristics
s-block	1, 2	ns^{1-2}	Reactive metals (except H, He); strongly electropositive; form ionic compounds; low IE; good reducing agents; colourless/diamagnetic ions; alkali metals and alkaline earth metals.
p-block	13–18	ns^2np^{1-6}	Mixture of metals, non-metals and metalloids; non-metallic character increases to the right; includes halogens and noble gases; variable oxidation states; many form covalent compounds.
d-block	3–12	$(n-1)d^{1-10}ns^{0-2}$	Transition metals; variable oxidation states; coloured ions; paramagnetic; catalytic activity; form complexes and alloys; hard, high m.p.
f-block	Lanthanoids, actinoids	$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$	Inner transition elements; similar properties within the series (lanthanoid contraction); actinoids are radioactive; coloured ions; complex formation.

Representative elements: s- and p-block (except group 18). **Noble gases:** group 18 (ns^2np^6 , He $1s^2$) with complete octets. **Transition elements:** d-block with partly filled d subshell in the atom or its common ions.

4.2 Atomic and Ionic Size

Definitions

- Atomic radius:** the distance from the centre of the nucleus to the outermost shell of electrons. It cannot be measured directly, as the electron cloud has no sharp boundary; it is estimated from internuclear distances in crystals/molecules.
- Covalent radius:** half of the internuclear distance between two identical atoms bonded by a single covalent bond, e.g. $r(\text{Cl}) = 99 \text{ pm} = \frac{1}{2}$ of Cl–Cl bond length (198 pm). For heteronuclear bonds: $d(\text{A–B}) = r(\text{A}) + r(\text{B})$ (Schomaker–Stevenson corrects for electronegativity difference).
- Van der Waals radius:** half of the internuclear distance between two adjacent non-bonded atoms of the same element in the solid state (closest approach). It is always larger than the covalent radius, e.g. Cl: 180 pm vs. 99 pm.
- Metallic radius:** half of the distance between nuclei of two adjacent atoms in a metallic crystal.
- Ionic radius:** the effective distance from the nucleus of an ion to the point up to which it exerts its influence in an ionic lattice. Pauling and Goldschmidt estimated values using ratio of radii and internuclear distances.

Order: van der Waals radius > metallic radius > covalent radius (for the same element).

Cations and anions

A **cation** is always smaller than its parent atom (loss of electrons, reduced electron–electron repulsion and greater effective nuclear charge per electron, and often loss of the whole outer shell), e.g. Na (186 pm) > Na^+ (95 pm). An **anion** is larger than its parent atom (gain of electrons increases repulsion with the same nuclear charge), e.g. Cl (99 pm) < Cl^- (181 pm). In **isoelectronic species** the size decreases with increasing nuclear charge: $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$.

Variation along a period (left to right)

Atomic size **decreases**. The number of shells remains the same, but the nuclear charge (Z) increases by one with each element, increasing the effective nuclear charge (Z_{eff}); the electrons are pulled closer to the nucleus. Noble gases show a larger apparent size because their radii are given as van der Waals radii.

Period 2	Li	Be	B	C	N	O	F
Covalent radius (pm)	152	111	88	77	70	66	64

Variation down a group

Atomic size **increases** as new electron shells are added; the increased screening by inner electrons outweighs the increase in nuclear charge. E.g. group 1: Li (152 pm) < Na (186) < K (227) < Rb (248) < Cs (265).

Special cases

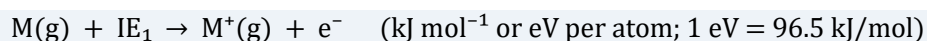
Transition elements: size decreases only slightly across a period due to the screening effect of d electrons.

Lanthanoid contraction (poor shielding by 4f electrons) causes 5d elements (Hf, Ta) to have almost the same radii as 4d elements (Zr, Nb); hence Zr and Hf are chemically very similar.

4.3 Ionization Energy (Ionization Enthalpy)

Definition and explanation

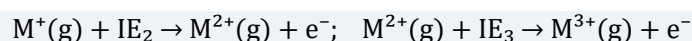
Ionization energy (IE) is the minimum amount of energy required to remove the most loosely bound (outermost) electron from an isolated gaseous atom in its ground state, converting it to a gaseous cation.



IE is always endothermic (positive). Low IE means the element readily forms a cation and is a strong reducing agent, so it is metallic in nature.

Successive ionization energies

The energies needed to remove the second, third ... electrons are the **successive ionization energies** ($IE_2, IE_3 \dots$).



$IE_{\{1\}} < IE_{\{2\}} < IE_{\{3\}} \dots$, because as electrons are removed the positive charge on the ion increases while the electron-electron repulsion decreases and the remaining electrons are held more tightly. A **sudden large jump** in IE signals the removal of an electron from an inner (closed) shell and thus indicates the number of valence electrons.

Element	IE_1	IE_2	IE_3	IE_4	Inference
Na (kJ/mol)	496	4562	6912	9543	Big jump after IE_1 : 1 valence electron, forms Na^+
Mg (kJ/mol)	738	1451	7733	10540	Big jump after IE_2 : 2 valence electrons, forms Mg^{2+}
Al (kJ/mol)	578	1817	2745	11577	Big jump after IE_3 : 3 valence electrons, forms Al^{3+}

Factors affecting ionization energy

- Atomic size:** IE decreases with increasing atomic size as the outer electron is farther from the nucleus and less strongly attracted.
- Nuclear charge:** IE increases with higher nuclear charge (greater attraction).
- Screening (shielding) effect:** inner-shell electrons shield the valence electrons from the nucleus; more shielding reduces IE.
- Penetration effect of orbitals:** penetration order $s > p > d > f$; an s electron is held more strongly than a p electron in the same shell, so $IE: s > p > d > f$.
- Electronic configuration (stability):** atoms with completely filled (s^2, p^6, d^{10}) or exactly half-filled (p^3, d^5) subshells are extra stable and have higher IE.

Variation along a period

IE **generally increases** from left to right because of increasing nuclear charge and decreasing atomic size. Noble gases have the highest IE in a period. There are **exceptions** in period 2 and 3:

- Be (900) > B (801):** Be has a stable fully filled $2s^2$; B has to lose a 2p electron, which is higher in energy and better shielded by 2s electrons.
- N (1402) > O (1314):** N has a stable half-filled $2p^3$ configuration; O ($2p^4$) has a paired electron whose repulsion makes removal easier.
- Similarly $Mg > Al$ and $P > S$.

Order in period 2: $Li < B < Be < C < O < N < F < Ne$

Variation down a group

IE **decreases** down a group because the atomic size increases and the screening effect of the added inner shells outweighs the increased nuclear charge, so the outer electron is held loosely. E.g. Li 520 > Na 496 > K 419 > Rb 403 > Cs 376 kJ/mol. In d-block the trend is irregular (IE of 5d is higher than 4d due to the lanthanoid contraction and poor shielding).

Applications of ionization energy to chemical behaviour

- **Metallic character:** elements with low IE readily lose electrons and are metals; high IE elements are non-metals.
- **Reducing power:** low IE means a strong reducing agent (alkali metals, e.g. Cs, are strongest).
- **Reactivity:** the reactivity of metals increases as IE decreases (K > Na > Li in water reactions); reactivity of non-metals relates to electron affinity.
- **Nature of bonding and oxidation state:** very high IE₂ for alkali metals makes +1 the only state; large IE for noble gases explains inertness.
- **Basic character of oxides:** low IE metals give strongly basic oxides/hydroxides (NaOH, KOH).
- **Valency from successive IE:** the sudden jump identifies the group.

4.4 Electron Affinity (Electron Gain Enthalpy)

Definition and explanation

Electron affinity (EA) is the amount of energy released when an extra electron is added to an isolated gaseous atom in its ground state to form a gaseous anion (uni-negative ion).



Electron gain enthalpy ($\Delta_{eg}H$) is the enthalpy change for the same process; it is negative when energy is released (exothermic) and positive when energy must be supplied. EA is numerically equal to $-\Delta_{eg}H$. A high positive EA (large negative $\Delta_{eg}H$) means the atom readily accepts an electron.

Successive electron affinities

The first EA is usually exothermic (positive EA). The addition of a **second electron** to a negative ion is opposed by electrostatic repulsion, so it is endothermic and requires energy: $O(g) + e^- \rightarrow O^-(g)$, $EA_1 = +141 \text{ kJ/mol}$; $O^-(g) + e^- \rightarrow O^{2-}(g)$, $EA_2 = -780 \text{ kJ/mol}$. Thus, O^{2-} is stable only in crystal lattices where lattice energy compensates for the energy required. Similarly S^{2-} and N^{3-} .

Factors affecting electron affinity

1. **Atomic size:** smaller atoms have higher EA (the incoming electron is nearer to the nucleus).
2. **Nuclear charge:** greater nuclear charge gives higher EA.
3. **Screening effect:** greater shielding by inner electrons decreases EA.
4. **Electronic configuration:** atoms with stable configurations (completely filled s^2 , half-filled p^3 , or noble gas) have very low or negative EA (Be, Mg, N, noble gases).

Variation along a period and in a group

Along a period: EA generally **increases** left to right because atomic size decreases and nuclear charge increases; halogens have the highest EA. **In a group:** EA generally **decreases** down the group as the size increases. **Anomaly:** the EA of second-period elements O and F is lower than that of S and Cl, respectively, because the very small 2p orbital leads to strong electron–electron repulsion when an electron is added.

Group 17	F	Cl	Br	I
EA (kJ/mol)	328	349	325	295
Order	Cl > F > Br > I			

Order of EA in group 16: S > Se > Te > O; **group 17:** Cl > F > Br > I. Noble gases have zero or positive $\Delta_{eg}H$ (negative EA) as the added electron must go into a new higher shell.

Applications of electron affinity to chemical behaviour

- **Non-metallic character and oxidising power:** high EA means a strong oxidising agent (halogens, especially Cl and F).
- **Nature of bonding:** elements with high EA readily form anions and ionic compounds with low IE metals.

- **Chemical reactivity:** the reactivity of non-metals depends on EA; halogens are most reactive.
- **Stability of anions:** helps explain why halide ions are stable but multi-charged anions (O^{2-}) exist only in lattices.
- **Calculation of lattice energy** through Born–Haber cycle uses EA values.

4.5 Electronegativity

Definition and explanation

Electronegativity (EN) is the tendency of an atom in a molecule (in a covalent bond) to attract the shared pair of electrons towards itself. It is a relative (dimensionless) property, not an energy. The most electronegative element is **fluorine (4.0 on Pauling scale)**; the least is caesium/francium (~ 0.7).

Difference from EA and IE: IE and EA are properties of isolated gaseous atoms (measurable, in kJ/mol), whereas EN refers to bonded atoms and is a relative scale.

Factors affecting electronegativity

- **Atomic size:** smaller atoms have higher EN (shared pair closer to nucleus).
- **Nuclear charge:** higher effective nuclear charge increases EN.
- **Hybridisation:** more s-character gives higher EN: sp (3.29) > sp^2 (2.75) > sp^3 (2.48) for carbon.
- **Oxidation state:** EN increases with increasing positive charge/oxidation state, e.g. $Fe^{3+} > Fe^{2+}$.
- **Charge on the atom and attached groups** also alter EN.

Variation along a period and in a group

Along a period: EN **increases** from left to right (greater Z_{eff} , smaller size). **Down a group:** EN **decreases** (increase in size).
E.g. period 2: Li 1.0, Be 1.5, B 2.0, C 2.5, N 3.0, O 3.5, F 4.0; group 17: F 4.0, Cl 3.0, Br 2.8, I 2.5.

Pauling's approach

Linus Pauling (1932) related electronegativity to bond energies. For a heteronuclear bond A–B, the actual bond energy E_{A-B} is greater than the geometric mean (or arithmetic mean) of the homonuclear bond energies E_{A-A} and E_{B-B} , the excess arising from the ionic contribution caused by the difference in electronegativity.

$$\Delta = E(A-B) - \sqrt{[E(A-A) \times E(B-B)]} \quad \text{and} \quad (\chi_A - \chi_B)^2 = \Delta / 96.5 \quad (E \text{ in kJ/mol})$$

Equivalently, $(\chi_A - \chi_B) = 0.208 \sqrt{\Delta}$, where Δ is in kcal/mol ($0.102 \sqrt{\Delta}$ with Δ in kJ/mol). Pauling assigned the value 4.0 to fluorine and 2.1 to hydrogen as reference points. Using the arithmetic mean instead: $\Delta' = E(A-B) - \frac{1}{2}[E(A-A) + E(B-B)]$, with $(\chi_A - \chi_B) = 0.208 \sqrt{\Delta'}$ (kcal) or $0.1017 \sqrt{\Delta'}$ (kJ).

Numerical example (Pauling's method)

Problem 1

Calculate the electronegativity of chlorine, given that the bond energies of H–H, Cl–Cl and H–Cl are 436, 242 and 431 kJ/mol respectively, and $\chi(H) = 2.1$.

Solution: Geometric mean = $\sqrt{436 \times 242} = \sqrt{105512} = 324.8$ kJ/mol.

$$\Delta = 431 - 324.8 = 106.2 \text{ kJ/mol.}$$

$$\chi_{Cl} - \chi_H = 0.102 \times \sqrt{106.2} = 0.102 \times 10.31 = 1.05.$$

$$\chi_{Cl} = 2.1 + 1.05 = \mathbf{3.15} \text{ (accepted value 3.0).}$$

Problem 2

The bond energies of H–H, Br–Br and H–Br are 436, 193 and 366 kJ/mol. Find $\chi(Br)$ if $\chi(H) = 2.1$.

Solution: $\sqrt{436 \times 193} = \sqrt{84148} = 290.1$; $\Delta = 366 - 290.1 = 75.9$ kJ/mol.

$$\chi_{Br} - \chi_H = 0.102 \times \sqrt{75.9} = 0.102 \times 8.71 = 0.89.$$

$$\chi_{Br} = 2.1 + 0.89 = \mathbf{2.99} \text{ } (\approx 2.8-3.0).$$

Problem 3

Bond energies: H–H = 104.2, F–F = 37.6, H–F = 135 kcal/mol. Find $\chi(F)$ with $\chi(H) = 2.1$.

Solution: $\sqrt{104.2 \times 37.6} = \sqrt{3917.9} = 62.6$; $\Delta = 135 - 62.6 = 72.4$ kcal/mol.

$$\chi_F - \chi_H = 0.208 \times \sqrt{72.4} = 0.208 \times 8.51 = 1.77; \chi_F = 2.1 + 1.77 = \mathbf{3.87} (\approx 4.0).$$

Mulliken's approach

R. S. Mulliken (1934) defined the electronegativity of an atom as the **average of its ionization energy and electron affinity**, since an atom that attracts electrons strongly would have a high IE (holds its own) and high EA (accepts more).

$$\chi_M = (IE + EA) / 2 \quad (\text{in eV}) \quad \text{and} \quad \chi_P = \chi_M / 2.8$$

Mulliken values (in eV) are converted to the Pauling scale by dividing by 2.8. **Example:** for fluorine IE = 17.42 eV and EA = 3.40 eV; $\chi_M = 10.41$ eV; $\chi_P = 10.41/2.8 = 3.7 (\approx 4.0)$. For Cl: IE = 13.0 eV, EA = 3.6 eV, $\chi_M = 8.3$ eV, $\chi_P = 8.3/2.8 = 3.0$.

Feature	Pauling scale	Mulliken scale
Basis	Bond (dissociation) energies	IE and EA of isolated atom
Formula	$\chi_A - \chi_B = 0.208\sqrt{\Delta} \text{ (kcal)} / 0.102\sqrt{\Delta} \text{ (kJ)}$	$\chi = (IE + EA)/2$
Reference	F = 4.0, H = 2.1	Converted by dividing by 2.8
Limitation	Needs bond energy data; applies only to bonded atoms	EA values not known accurately for many elements
Type	Thermochemical, relative	Absolute

Applications of electronegativity to bond properties

(a) Percent ionic character. A covalent bond between two different atoms is polar. As the electronegativity difference ($\Delta\chi$) increases, ionic character increases. Hannay–Smyth equation:

$$\% \text{ ionic character} = 16 (\chi_A - \chi_B) + 3.5 (\chi_A - \chi_B)^2$$

Pauling's relation: $\% \text{ ionic character} = [1 - \exp(-\frac{1}{4}(\chi_A - \chi_B)^2)] \times 100$. A bond with $\Delta\chi = 1.7$ has ~50% ionic character; $\Delta\chi > 1.7$ means predominantly ionic, < 1.7 predominantly covalent. Example: HF ($\Delta\chi = 1.9$): ~59%; HCl ($\Delta\chi = 0.9$): ~18%; NaCl ($\Delta\chi = 2.1$): ~67%; CsF: ~92%.

Worked example

For H–Cl with $\chi_H = 2.1$ and $\chi_{Cl} = 3.0$: $\Delta\chi = 0.9$. $\% \text{ ionic} = 16(0.9) + 3.5(0.81) = 14.4 + 2.8 = \mathbf{17.2\%} (\approx 17\text{--}18\%)$.

(b) Bond length. The actual bond length is shorter than the sum of the covalent radii when the electronegativity difference is large (Schomaker–Stevenson): $d(A-B) = r_A + r_B - 0.09 |\chi_A - \chi_B|$ (in Å). Greater polarity gives extra electrostatic attraction and a shorter bond. E.g. observed C–F, C–O bonds are shorter than the sum of radii.

(c) Bond angle. In molecules of the type AX_3 (NH_3 , NF_3) or AH_2 (H_2O , H_2S) the bond angle depends on the electronegativity of the central atom and the attached atoms. If the central atom is highly electronegative (N in NH_3), bonding pairs are pulled toward it, so pair–pair repulsion increases and the angle widens: NH_3 (107°) $>$ PH_3 (93.5°) $>$ AsH_3 (92°); H_2O (104.5°) $>$ H_2S (92°) $>$ H_2Se (91°). If the surrounding atoms are highly electronegative, the bonding pairs are drawn away from the central atom, reducing repulsion and decreasing the angle: NH_3 (107°) $>$ NF_3 (102°); OH_2 (104.5°) $>$ OF_2 (103°).

Other applications of electronegativity

- **Polarity and dipole moment:** larger $\Delta\chi$ gives a larger bond dipole.
- **Nature of bond:** $\Delta\chi = 0$ non-polar covalent; $0 < \Delta\chi < 1.7$ polar covalent; $\Delta\chi > 1.7$ ionic.
- **Metallic vs. non-metallic character:** metals have $EN < 2$; non-metals have $EN > 2$; metalloids ~1.8–2.2.
- **Oxidising and reducing character, acidity of oxo-acids** ($HClO_4 > HClO_3 > HClO$), and bond strengths.
- **Hydrogen bonding** occurs when H is bonded to highly electronegative N, O, F.

Property	Along a period (L→R)	Down a group
Atomic size	Decreases	Increases
Ionization energy	Increases (with exceptions)	Decreases
Electron affinity	Increases (with exceptions)	Decreases (O, F anomaly)

Property	Along a period (L→R)	Down a group
Electronegativity	Increases	Decreases
Metallic character	Decreases	Increases
Reducing power	Decreases	Increases
Oxidising power	Increases	Decreases
Basicity of oxides	Decreases	Increases

Quick Revision – Unit IV

1. Modern periodic law: properties are a periodic function of atomic number.
2. Size: decreases across a period, increases down a group; cation < atom < anion.
3. IE: increases across; exceptions Be > B, N > O. Big jump in successive IE shows the valence shell.
4. EA: highest for Cl; second EA is always endothermic.
5. Pauling: $\chi_A - \chi_B = 0.102\sqrt{\Delta}$ (kJ); Mulliken: $\chi = (IE+EA)/2$.
6. % ionic character = $16\Delta\chi + 3.5(\Delta\chi)^2$.

Important Questions for Practice

Unit I

1. Define electrophile and nucleophile with two examples each.
2. Explain the inductive effect and its application to the acidic strength of carboxylic acids.
3. What is hyperconjugation? Explain stability of alkenes and carbocations on its basis.
4. Compare homolytic and heterolytic fission.
5. Discuss the structure and stability of carbocation, carbanion and free radical; write short notes on carbene, nitrene and benzyne.

Unit II

1. Explain the structure of benzene with its orbital picture. Why is Kekulé structure inadequate?
2. State and explain Hückel's rule with examples of aromatic, antiaromatic and homoaromatic compounds.
3. Write the mechanism of nitration and halogenation of benzene.
4. Explain Friedel–Crafts alkylation and acylation with mechanism. State limitations.
5. Explain why –OH is o,p-directing, –NO₂ is m-directing, and chlorine is deactivating yet o,p-directing.

Unit III

1. Describe two methods of preparing ethylene glycol. What happens when it is treated with Pb(OAc)₄ and P₂O₅?
2. How is glycerol prepared from oils/fats and from propene? Give its reactions with nitric acid and acetyl chloride.
3. Write two methods of preparing ethylene oxide.
4. Explain ring opening of propylene oxide in acidic and basic medium and with a Grignard reagent.
5. Why is phenol more acidic than ethanol? Write the mechanism of Reimer–Tiemann, Fries rearrangement and Kolbe's reaction.

Unit IV

1. State the modern periodic law; define atomic, covalent, ionic and van der Waals radii.
2. Define ionization energy. Explain the factors affecting it and why Be > B, N > O.
3. Define electron affinity. Why is the EA of chlorine greater than fluorine?
4. Explain Pauling's and Mulliken's approaches to electronegativity.
5. Solve Pauling electronegativity numericals; explain how electronegativity affects % ionic character, bond length and bond angle.