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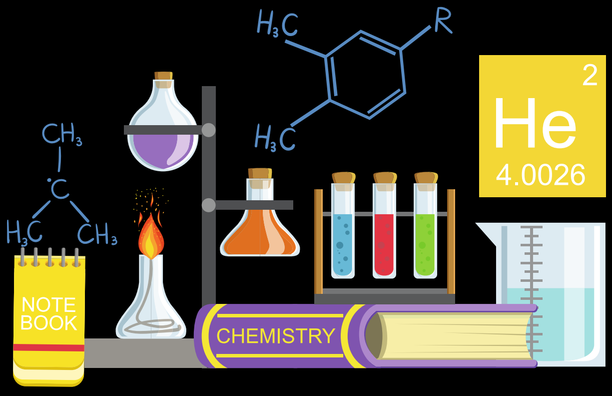

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Spectroscopy

The modern organic chemist used spectroscopic methods, each giving information about a molecule's composition and framework. This integrated approach, often termed "spectroscopic structure determination," allows for the complete characterization of even highly complex molecule. The primary techniques include Mass Spectrometry (MS), Infrared (IR) Spectroscopy, Ultraviolet-Visible (UV-Vis) Spectroscopy, and Nuclear Magnetic Resonance (NMR) Spectroscopy. Together, these methods give information about molecular analysis: determining molecular weight and formula (MS), identifying functional groups (IR), detecting conjugated π-electron systems (UV-Vis), and mapping the carbon-hydrogen framework (NMR).

1. NMR Spectroscopy

Introduction to NMR Spectroscopy

Definition:

Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical technique that exploits the magnetic properties of certain atomic nuclei to determine the type, number, and relative positions of atoms in organic molecules. It provides detailed information about molecular structure, dynamics, and chemical environment.

1.1 Historical Background:

The phenomenon of NMR was discovered independently in 1946 by Felix Bloch (Stanford University) and Edward Purcell (Harvard University), for which they shared the Nobel Prize in Physics in 1952. The initial application was in physics for measuring nuclear magnetic moments. Its potential for chemistry was realized in the early 1950s when it was discovered that the resonance frequency of a nucleus depends on its chemical environment—the chemical shift. The development of Fourier Transform NMR (FT-NMR) and multidimensional NMR techniques by Richard R. Ernst (for which he received the Nobel Prize in Chemistry in 1991) dramatically increased the sensitivity, speed, and information content of NMR, enabling its application to complex biological macromolecules. Today, NMR is indispensable in organic chemistry, biochemistry (for protein structure determination), pharmaceuticals, materials science, and medicine (as the basis for Magnetic Resonance Imaging, MRI).

1.2 Basic Principles of NMR

Fundamental Principles: Nuclear Spin and Resonance

Only certain atomic nuclei possess the property of **nuclear spin**, described by the spin quantum number (I). Nuclei with an odd mass number (e.g., ^{1}H, ^{13}C, ^{19}F, ^{31}P) have half-integral spin (I = 1/2, 3/2...). Nuclei with even mass number but odd atomic number (e.g., ^{2}H, ^{14}N) have integral spin (I = 1, 2...). Nuclei with even mass and even atomic numbers (e.g., ^{12}C, ^{16}O) have I = 0 and are NMR inactive. For organic chemists, the most important NMR-active nuclei are ^{1}H (I=1/2, 99.98% natural abundance) and ^{13}C (I=1/2, 1.1% natural abundance).

A nucleus with spin $I \neq 0$ possesses a magnetic moment. In the absence of an external magnetic field, these nuclear magnets are randomly oriented. When placed in a strong, static external magnetic field ($\mathbf{B_0}$), the nuclear spins adopt quantized orientations relative to the field direction. The number of possible orientations is given by $\mathbf{2I + 1}$. For a spin-½ nucleus like ^{1}H or ^{13}C, there are two orientations: a lower energy state aligned with $\mathbf{B_0}$ ($m_I = +\frac{1}{2}$) and a higher energy state opposed to $\mathbf{B_0}$ ($m_I = -\frac{1}{2}$). The energy

Vicinal protons (on adjacent carbons): 2–18 Hz

Long-range coupling in unsaturated systems: smaller J values

Pascal's Triangle

Predicts relative intensities of peaks in a multiplet.

For n neighboring protons, intensities correspond to binomial coefficients.

Number of Neighbors (n)	Multiplicity	Intensity Pattern
0	Singlet	1
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Quintet	1:4:6:4:1

1.6 NMR Instrumentation

Key Components

1. **Sample Holder:**
   Glass or quartz tube (=18 cm long,0.5 cm diameter).
   Chemically inert and transparent to RF.
2. **Magnet:**
   Magnet provides high homogeneous field (measured in Tesla); instruments are often referred to by 60–1000 MHz (^{1}H frequency)." Superconducting magnets used in modern spectrometers.
3. **RF Transmitter:**
   Generates short, powerful pulses of radio waves.
4. **RF Receiver:**
   Detects emitted RF signals from relaxing nuclei.
5. **Sweep Generator**
   Varies magnetic field or frequency to bring nuclei into resonance.
6. **Detector and Computer System:**
   Amplifies, processes, and records signals.
   Fourier Transform (FT) converts time-domain data to frequency-domain spectrum.

Solvents in NMR

Must be deuterated to avoid interference from solvent protons.

Common solvents: $CDCl_3$, D_2O, DMSO-d_6, acetone-d_6, benzene-d_6.

Choice depends on solubility and chemical shift range.

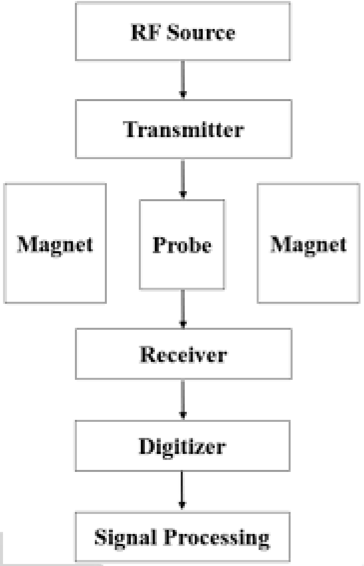


Diagram: A simple NMR spectrometer working

1.7 Applications of NMR Spectroscopy

1. **Structure Elucidation:**
   Determination of molecular structure, stereochemistry, and conformation.
2. **Quantitative Analysis:**
   Integration of signals gives proton ratios.
3. **Dynamic Studies:**
   Investigation of reaction kinetics, conformational exchange, and hydrogen bonding.
4. **Biomolecular NMR:**
   Protein folding, ligand binding, and metabolic profiling.
5. **Material Science:**
   Polymer characterization, porosity studies, and surface chemistry.
6. **Medical Imaging (MRI):**
   Non-invasive imaging using NMR principles.

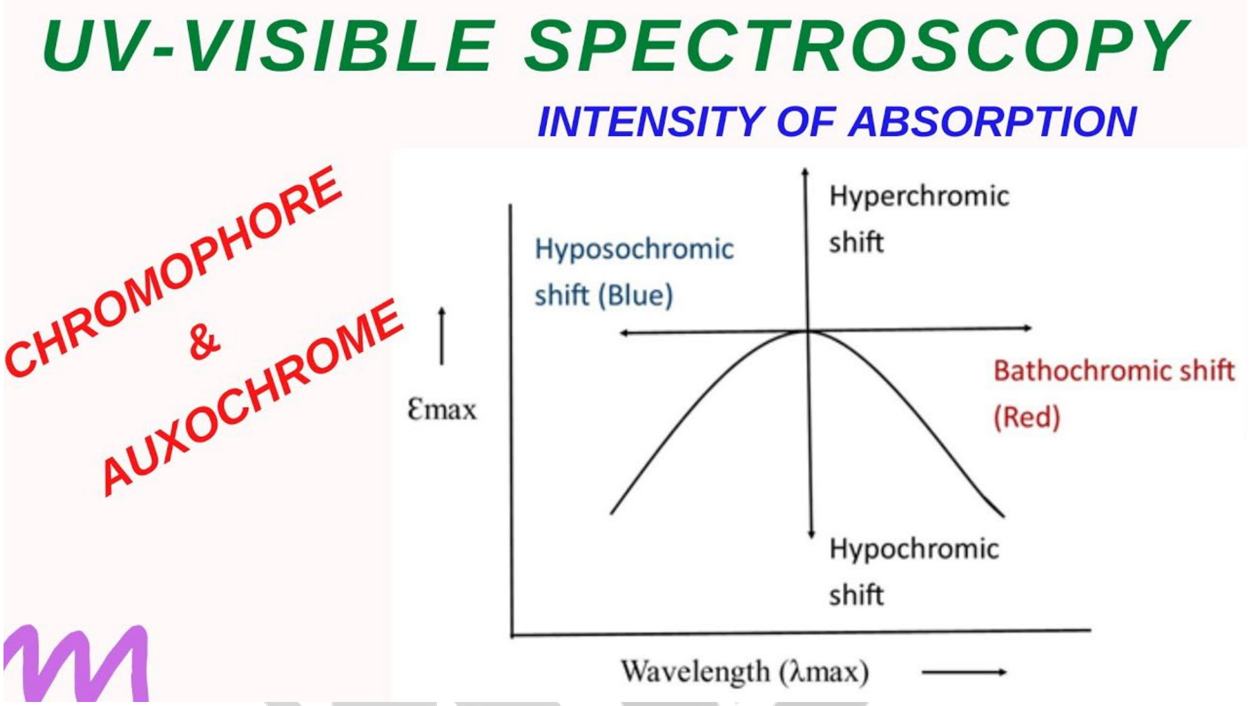
2. UV-Visible Spectroscopy

2.1 Introduction to UV-Visible Spectroscopy

Ultraviolet-Visible spectroscopy involves the promotion of electrons from ground-state molecular orbitals to higher-energy excited states. The energy required for these transitions falls in the ultraviolet (typically 190-400 nm) and visible (400-800 nm) regions of the electromagnetic spectrum. While less specific for detailed structural elucidation than IR or NMR, UV-Vis spectroscopy is exquisitely sensitive to the presence of conjugated π-electron systems, providing information about the extent of conjugation, stereochemistry, and allowing for highly accurate quantitative analysis.

Principles of Electronic Transitions

In molecules, electrons occupy molecular orbitals (MOs) with specific energies. The absorption of a photon of appropriate energy ($E = h\nu = hc/\lambda$) can promote an electron from a filled orbital (e.g., bonding



Chromophores and Auxochromes

chromophore

is the part of a molecule responsible for its UV-Vis absorption—A chromophore is a group capable of **$\pi \rightarrow \pi^*$** or **$n \rightarrow \pi^*$** electronic transitions with lone pairs. (e.g., C=C, C=O, C≡N, NO_2, aromatic rings).

auxochrome is a functional group attached to a chromophore that does not itself absorb in the UV-Vis region but modifies the absorption of the chromophore, usually causing a bathochromic shift and hyperchromic effect (increase in intensity). Auxochromes typically contain lone pairs (e.g., -OH, $-NH_2$, -OR) that can conjugate with the chromophore's π-system, extending the conjugation and lowering the HOMO-LUMO gap.

The Beer-Lambert Law and Quantitative Analysis

UV-Vis spectroscopy is the primary technique for quantitative analysis in solution. The **Beer-Lambert Law** (or Beer's Law) states that the absorbance (A) of a solution is directly proportional to the concentration (c) of the absorbing species and the path length (l) of the sample cell: **$A = \varepsilon c l$**.

Absorbance (A) is defined as $A = \log_{10}(I_0/I)$, where I_0 is the intensity of incident light and I is the intensity of transmitted light.

Molar Absorptivity (ε) is a constant characteristic of the substance at a given wavelength, expressed in $L\ mol^{-1}\ cm^{-1}$. It is a measure of how strongly a compound absorbs. A high ε value indicates a high probability of the electronic transition.

Path length (l) is typically 1 cm for standard cuvettes.

The Beer-Lambert Law assumes: monochromatic light, non-interacting absorbing species, a homogeneous medium, and no scattering or fluorescence. Deviations occur at high concentrations (>0.01 M) or if chemical associations (e.g., dimerization) occur.

Empirical Rules for Predicting λ_max: Woodward-Fieser Rules

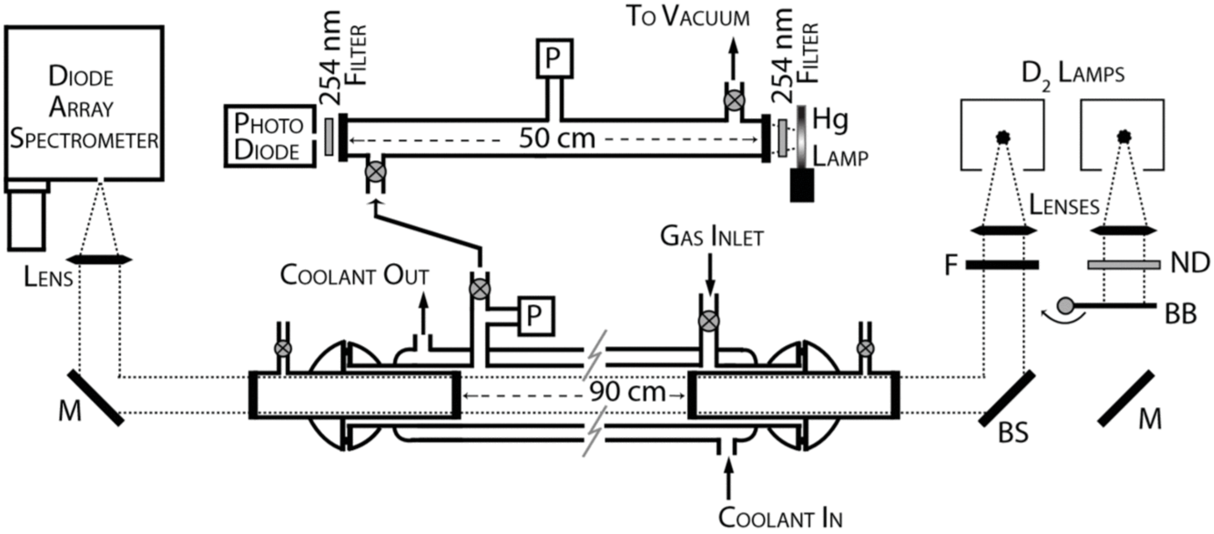


Diagram A sample instrument UV (CCD) VIS Spectrometer

Types of Spectrophotometers

Single Beam: One light path; requires blank correction.

Double Beam: Splits light into sample and reference paths for real-time correction.

2.7 Solvent Selection

Must be transparent in the region of interest.

Common solvents: water, ethanol, hexane, acetonitrile.

Polar solvents may reduce fine structure due to hydrogen bonding.

2.8 Applications of UV-Visible Spectroscopy

1. **Qualitative Analysis:**
   Identification of functional groups and conjugation.
2. **Quantitative Analysis:**
   Determination of concentration using calibration curves.
3. **Chemical Kinetics:**
   Monitoring reaction rates by absorbance changes.
4. **Detection of Impurities:**
   Sensitive to aromatic or conjugated impurities.
5. **Structural Studies:**
   Detection of isomerism, tautomerism, and complex formation.
6. **Biological Applications:**
   Protein and nucleic acid quantification, enzyme assays.

3. Comparison of NMR and UV-Visible Spectroscopy

Feature	NMR Spectroscopy	UV-Visible Spectroscopy
Principle	Nuclear spin transitions in magnetic field	Electronic transitions
Radiation Used	Radio waves (MHz)	UV-Visible light (nm)

C. Electrospray Ionization (ESI) & MALDI

Soft ionization methods used for large, thermally labile molecules (e.g., proteins).

Produce protonated molecules $[M^{+}H]^{+}$ with minimal fragmentation.

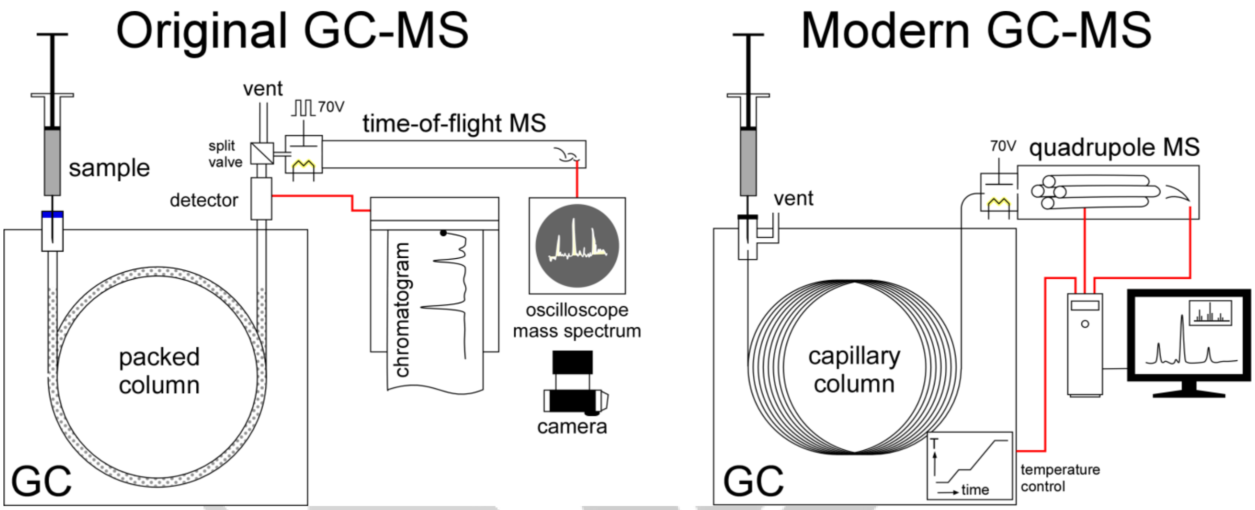


Diagram **A sample GC-MS**

Mass Analyzers

A. Magnetic Sector Analyzer

Ions separated by magnetic field based on m/z.

Used in high-resolution MS for exact mass measurement.

B. Quadrupole Analyzer

Four parallel rods with oscillating electric field filter ions based on m/z

Fast scanning, robust, commonly used in GC-MS.

C. Time-of-Flight (TOF) Analyzer

Ions accelerated to same kinetic energy; separation based on velocity.

Lighter ions reach detector first.

High mass range, used in MALDI-TOF for biomolecules.

D. Ion Trap Analyzer

Ions trapped in electromagnetic field and sequentially ejected based on m/z.

Compact, sensitive, allows MS/MS experiments.

4.3 Interpreting Mass Spectra

Molecular Ion (M^{+}): Peak corresponding to intact ionized molecule.

Base Peak: Most intense peak in spectrum (assigned 100% abundance).

Isotopic Peaks:

M+1 peak arises primarily from **^{13}C**.

M+2peak characteristic of Cl or Br (isotopic patterns).

3. Structural elucidation through fragmentation analysis.
4. Quantitative analysis in combination with chromatography.
5. Study of biomolecules (proteins, peptides, oligonucleotides).

Topic Wise One Liners: Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy

1. **Nuclear Magnetic Resonance (NMR) spectroscopy** is an analytical technique that exploits the magnetic properties of certain atomic nuclei to determine molecular structure, dynamics, and chemical environment.
2. NMR is based on the absorption of **radiofrequency (RF) radiation** by nuclei placed in a strong static magnetic field, causing transitions between nuclear spin energy levels.
3. The phenomenon was independently discovered in 1946 by **Felix Bloch** and **Edward Purcell**, who shared the **Nobel Prize in Physics in 1952**.
4. **Richard R. Ernst** received the **Nobel Prize in Chemistry in 1991** for developing Fourier-transform and multi-dimensional NMR techniques.
5. NMR is essential for **structure elucidation** in organic, inorganic, organometallic, and biochemistry (proteins, nucleic acids, metabolites).
6. It is a **non-destructive technique** suitable for solids, liquids, and solutions, and forms the basis of **Magnetic Resonance Imaging (MRI)**.
7. Only nuclei with a **non-zero nuclear spin ($I \neq 0$)** possess a magnetic moment and are NMR-active.
8. The **spin quantum number (I)** depends on mass and atomic numbers: odd mass (half-integral spin: ^{1}H, ^{13}C, ^{19}F, ^{31}P), even mass & even atomic number (I=0, NMR inactive: ^{12}C, ^{16}O), even mass & odd atomic number (integral spin: ^{2}H, ^{14}N).
9. In an external magnetic field (**B_0**), nuclear spins adopt **$2I + 1$** quantized orientations.
10. For spin-½ nuclei (e.g., ^{1}H, ^{13}C), two energy states exist: +½ (aligned with B_0, lower energy) and –½ (opposed to B_0, higher energy).
11. **Resonance** occurs when the applied RF frequency matches the energy difference (**ΔE**) between these spin states.
12. The **Larmor frequency (ν)** is given by **$\nu = (\gamma B_0) / 2\pi$**, where γ is the gyromagnetic ratio (nucleus-specific).
13. After excitation, nuclei return to equilibrium via **relaxation processes**: **spin-lattice (T_1)** and **spin-spin (T_2) relaxation**.
14. **T_1 (longitudinal relaxation)** involves energy transfer to the surroundings (lattice).
15. **T_2 (transverse relaxation)** involves loss of phase coherence among spins, affecting signal linewidth.
16. **^{1}H NMR (Proton NMR)** analyzes hydrogen nuclei, providing information on proton count, chemical environment, and neighboring protons (0–12 ppm range).
17. **^{13}C NMR** analyzes carbon-13 nuclei (natural abundance 1.1%), has a broader chemical shift range (0–220 ppm), and lower sensitivity than ^{1}H NMR.
18. ^{13}C NMR spectra are usually recorded in **proton-decoupled mode** to simplify spectra into singlets for each carbon.
19. **Multinuclear NMR** includes ^{19}F (fluorinated compounds), ^{31}P (biochemistry, organophosphorus chemistry), and ^{15}N (peptides, proteins) NMR.

Practice MCQs

1. Which scientist shared the Nobel Prize in Physics in 1952 for the discovery of NMR?

A) Richard R. Ernst
B) Felix Bloch and Edward Purcell
C) Robert Woodward
D) Louis Fieser

Answer: Felix Bloch and Edward Purcell

2. For a nucleus to be NMR active, it must have:

A) An even atomic number
B) A spin quantum number $I = 0$
C) A non-zero spin ($I \neq 0$)
D) An even mass number

Answer: A non-zero spin ($I \neq 0$)

3. The reference compound used in both ^1H and ^{13}C NMR, assigned 0 ppm, is:

A) Deuterated chloroform
B) Benzene
C) Tetramethylsilane (TMS)
D) Dimethyl sulfoxide

Answer: Tetramethylsilane (TMS)

4. A proton with three equivalent neighboring protons will show a signal split into:

A) A triplet
B) A quartet
C) A doublet
D) A quintet

Answer: A quartet

5. The distance between peaks in an NMR multiplet, measured in Hz and independent of magnetic field strength, is the:

A) Chemical shift
B) Larmor frequency
C) Coupling constant
D) Gyromagnetic ratio

Answer: Coupling constant

6. Which ionization method in mass spectrometry is considered "soft" and commonly used for proteins and peptides?

A) Electron Impact (EI)
B) Chemical Ionization (CI)
C) Electrospray Ionization (ESI)
D) Flame Ionization

Answer: Electrospray Ionization (ESI)

7. According to the Nitrogen Rule in mass spectrometry, a compound with an even number of nitrogen atoms will have a molecular ion with:

A) An odd nominal mass
B) An even nominal mass
C) A fractional mass
D) No molecular ion

Answer: An even nominal mass

8. The Beer-Lambert Law states that absorbance is directly proportional to:

A) Incident light intensity only
B) Path length and concentration
C) Wavelength only
D) Temperature and pressure

Answer: Path length and concentration

9. A shift in UV-Vis absorption to a longer wavelength is called a:

A) Hypsochromic shift
B) Hyperchromic shift
C) Bathochromic shift
D) Hypochromic shift

Answer: Bathochromic shift

10. Which electronic transition is forbidden and typically weak in intensity?

A) $\sigma \rightarrow \sigma^*$
B) $n \rightarrow \sigma^*$
C) $\pi \rightarrow \pi^*$
D) $n \rightarrow \pi^*$

Answer: $n \rightarrow \pi^*$

11. The fingerprint region in IR spectroscopy is found in the range:

A) 4000–2500 cm^{-1}
B) 2500–2000 cm^{-1}
C) 1500–500 cm^{-1}
D) 2000–1500 cm^{-1}

Answer: 1500–500 cm^{-1}

Chromatography

Introduction to Chromatography

Chromatography is a powerful physical separation method used to resolve, identify, and quantify individual components (analytes) within complex mixtures. It operates on the fundamental principle of differential distribution of analytes between two immiscible phases:

a **stationary phase** and a **mobile phase**. Separation occurs due to differences in the affinity of analytes for these phases, based on physicochemical properties such as polarity, size, charge, and volatility. This technique is necessary in fields like pharmaceuticals, environmental monitoring, forensics, food safety, and biochemical research due to its high sensitivity, selectivity, and ability to handle complex matrices.

Historical Development and Significance

The term **chromatography** is derived from the Greek words *chroma* (color) and *graphein* (to write). The technique originated in 1901 from the work of Russian botanist **Mikhail Tsvett**, who separated plant pigments like chlorophylls and carotenoids by passing a plant extract through a column packed with calcium carbonate, observing distinct colored bands. This foundational experiment demonstrated the principle of differential solute migration. In 1940 with the development of **partition chromatography** by **Archer John Porter Martin** and **Richard Laurence Millington Synge**, for which they were awarded the **Nobel Prize in Chemistry in 1952**. Their work introduced the concept of a stationary liquid phase supported on a solid, leading to paper chromatography. Subsequent decades saw the evolution of **gas chromatography (GC)** in the 1950s, **high-performance liquid chromatography (HPLC)** in the 1960s, and hyphenated techniques like GC-MS and LC-MS. Today, chromatography is a cornerstone of analytical science.

Fundamental Principles and Terminology

In chromatography, the **stationary phase** is fixed in place (e.g., a solid adsorbent or a liquid coated on a solid support), while the **mobile phase** (a liquid or gas) moves through or over it, carrying the analytes. Separation is based on **differential partitioning** of analytes between these two phases, governed by their chemical and physical properties.

Key Chromatographic Parameters

Retention Time (t_r): The time taken for a specific analyte to travel from the injector to the detector. It is a primary identifying characteristic under constant conditions.

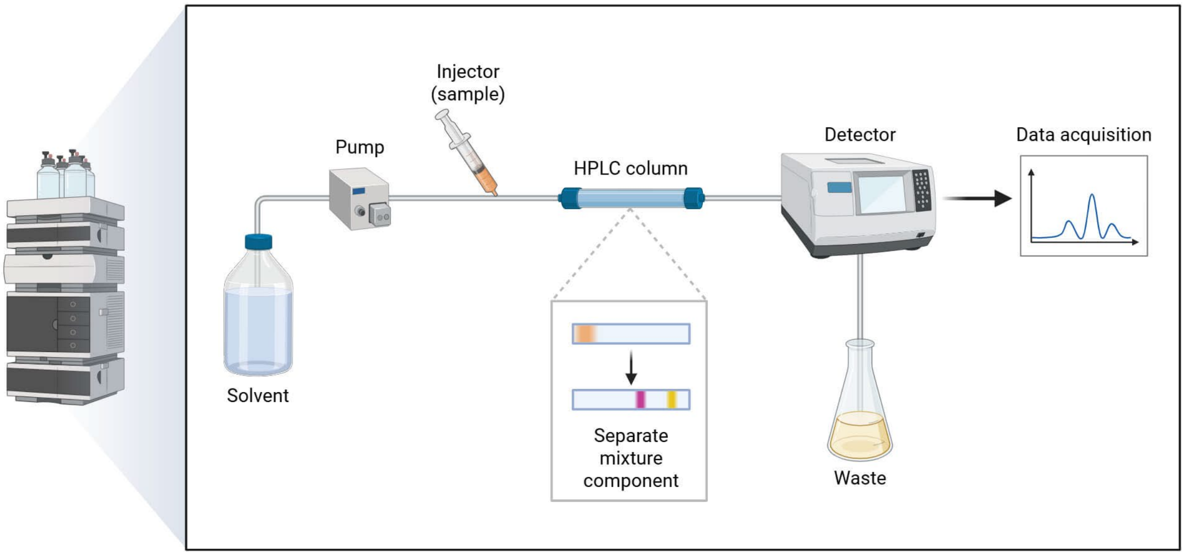
Hold-up Time (t_m or t_0): The retention time of a non-retained compound, representing the time for the mobile phase to traverse the column (also called dead time).

Adjusted Retention Time (t_r'): The net time an analyte spends interacting with the stationary phase, calculated as $t_r' = t_r - t_m$.

Retention Factor (Capacity Factor, k'): A dimensionless measure of retention, defined as $k' = (t_r - t_m)/t_m = t_r'/t_m$. It indicates how much longer an analyte is retained relative to an unretained substance. A k' value between 1 and 10 is generally desirable.

Distribution/Partition Coefficient (K): The fundamental equilibrium constant describing analyte distribution at a specific temperature: $K = C_s/C_m$, where C_s is the concentration in the stationary phase and C_m is the concentration in the mobile phase. It is related to the retention factor by the **phase ratio ($\beta = V_s/V_m$)**: $k = K/\beta$.

High Performance Liquid Chromatography (HPLC)

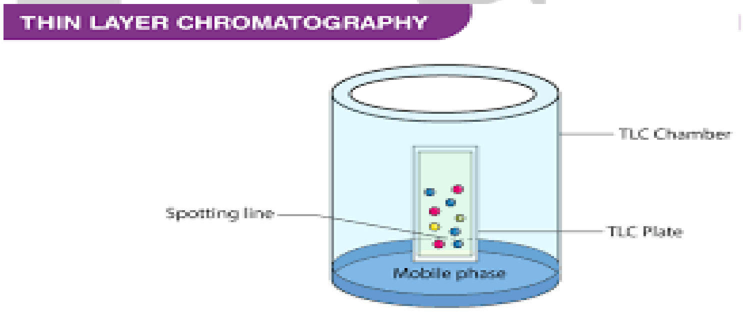


3. Thin-Layer Chromatography (TLC) & Paper Chromatography (PC)

These are simple, rapid, and cost-effective planar techniques primarily used for qualitative analysis and reaction monitoring.

In **TLC**, a **stationary phase:**

Silica gel (SiO_2) or Alumina (Al_2O_3)



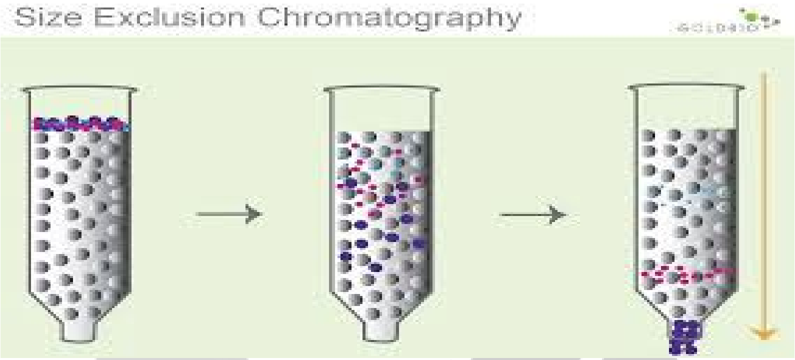
Mobile phase:

Organic solvent mixture

The sample is spotted, and the mobile phase ascends via capillary action.

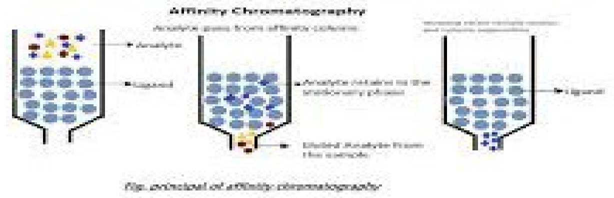
In **PC**, the stationary phase is hydrophilic filter paper.

SEC separates molecules based on hydrodynamic volume/size using a porous stationary phase. Larger molecules cannot enter pores and elute first (void volume). Smaller molecules penetrate pores and elute later. It is used for polymer molecular weight distribution and protein purification.



6. Affinity Chromatography

This technique uses highly specific biological interactions (e.g., antibody-antigen) for purification. The target molecule is eluted by changing conditions (pH, ionic strength) to disrupt the binding.



7. Supercritical Fluid Chromatography (SFC)

SFC uses a supercritical fluid (often CO_2) as the mobile phase, combining advantages of GC (high diffusivity) and LC (ability to dissolve non-volatiles). It is particularly useful for chiral separations and analysis of thermally labile compounds.

Topic Wise One Liners: Chromatography

History and Basics

1. **Mikhail Tsvett** is credited with inventing chromatography in 1901 while separating plant pigments.
2. The term **chromatography** is derived from Greek words meaning "color writing."
3. **Archer Martin and Richard Synge** won the 1952 Nobel Prize in Chemistry for developing **partition chromatography**.
4. Chromatography is a **physical separation method** where components distribute between a **stationary phase** and a **mobile phase**.
5. The **stationary phase** is fixed and can be a solid, a liquid supported on a solid, or a gel.
6. The **mobile phase** flows through the stationary phase and can be a **gas, liquid, or supercritical fluid**.
7. Separation occurs due to differences in analyte **affinity for the stationary phase** versus **solubility in the mobile phase**.
8. Components with greater affinity for the stationary phase **elute later** (have longer retention times).
9. The technique is indispensable in **pharmaceuticals, environmental science, forensics, and biochemistry**.
10. A primary limitation of analytical chromatography is that it is predominantly a **laboratory-scale** technique.

Fundamental Parameters

11. **Retention time (t_r)** is the time from sample injection to the peak maximum at the detector.
12. **Hold-up time (t_m or t_0)** is the elution time of an **unretained compound**, representing mobile phase travel time.
13. **Adjusted retention time (t_r')** = $t_r - t_m$, representing the net time spent in the stationary phase.
14. The **retention factor (k')** = $(t_r - t_m)/t_m$; it is a dimensionless measure of how long a compound is retained.
15. A k' value between **1 and 10** is generally desirable for a balanced separation.
16. The **distribution/partition coefficient (K)** = C_s/C_m, the equilibrium constant for analyte distribution between phases.
17. The **phase ratio (β)** = V_m/V_s; the retention factor is related to the partition coefficient by **$k' = K/\beta$**.
18. The **selectivity factor (α)** = k'_2/k'_1 (for $k'_2 > k'_1$); α must be **greater than 1.0** for separation to occur.
19. Selectivity is changed by altering the **stationary phase chemistry, temperature** (GC), **or mobile phase composition** (LC).
20. **Resolution (R_s)** = $2\Delta t_r/(W_{b1}+W_{b2})$; it quantifies the separation between two adjacent peaks.
21. An R_s value of **1.5** represents approximately **99.7% baseline separation**.
22. The **fundamental resolution equation** is $R_s = (\sqrt{N}/4) \times ((\alpha-1)/\alpha) \times (k'/(1+k'))$.
23. **Peak asymmetry factor (A_s)** = b/a at 10% peak height; $A_s = 1$ indicates a symmetric peak.

Column Efficiency and Band Broadening

24. **Plate Theory** models the column as a series of discrete theoretical plates where equilibrium occurs.
25. The **number of theoretical plates (N)** = $16(t_r/W_b)^2$; it is a measure of **column efficiency**.
26. **Plate height (HETP or H)** = L/N; a smaller H indicates a more efficient column.
27. **Reduced plate height (h)** = H/d_p, allowing comparison of columns with different **particle sizes**.
28. The **van Deemter equation**, $H = A + B/u + C \cdot u$, describes the relationship between plate height and mobile phase linear velocity.

Practice MCQs

Q. Who is credited with the invention of chromatography in 1901?

A) Archer Martin
B) Richard Synge
C) Mikhail Tsvett
D) James Lovelock

Answer: C) Mikhail Tsvett

Q. The term "chromatography" is derived from Greek words meaning:

A) Color separation
B) Color writing
C) Mixture analysis
D) Pigment study

Answer: B) Color writing

Q. For which development did Archer Martin and Richard Synge receive the Nobel Prize in Chemistry in 1952?

A) Invention of Gas Chromatography
B) Development of Partition Chromatography
C) Discovery of Adsorption Chromatography
D) Invention of the Mass Spectrometer

Answer: B) Development of Partition Chromatography

Q. In chromatography, the phase that moves through or over the stationary phase is called the:

A) Eluent
B) Analyte phase
C) Mobile phase
D) Dynamic phase

Answer: C) Mobile phase

Q. The time between sample injection and the maximum of the analyte peak is known as:

A) Void time
B) Retention time
C) Dead time
D) Elution time

Answer: B) Retention time

Q. The retention factor (k) is calculated as:

A) t_r/t_m
B) $(t_r - t_m)/t_m$
C) t_m/t_r
D) $t_r \times t_m$

Answer: B) $(t_r - t_m)/t_m$

Q. The ratio of the concentration of a solute in the stationary phase to its concentration in the mobile phase at equilibrium is the:

A) Retention factor
B) Selectivity factor
C) Distribution coefficient
D) Partition ratio

Answer: C) Distribution coefficient

Q. The ability of a chromatographic system to separate two analytes is measured by:

A) Retention factor (k)
B) Resolution (R_s)
C) Plate number (N)
D) Void volume

Answer: B) Resolution (R_s)

Q. Which of the following chromatographic techniques uses a gaseous mobile phase?

A) HPLC
B) TLC
C) GC
D) SEC

Answer: C) GC

Q. Separation based on differential adsorption of analytes onto a solid surface describes:

A) Partition Chromatography
B) Ion-Exchange Chromatography
C) Adsorption Chromatography
D) Affinity Chromatography

Answer: C) Adsorption Chromatography

Q. In Partition Chromatography, separation is based on differences in:

A) Molecular charge
B) Molecular size
C) Solubility in two phases
D) Adsorption strength

Answer: C) Solubility in two phases

Biochemistry

Introduction to Biomolecules

Definition: Biomolecules are the organic molecules that form the basis of life, produced by living organisms. They are essential for cellular structure, function, and metabolism.

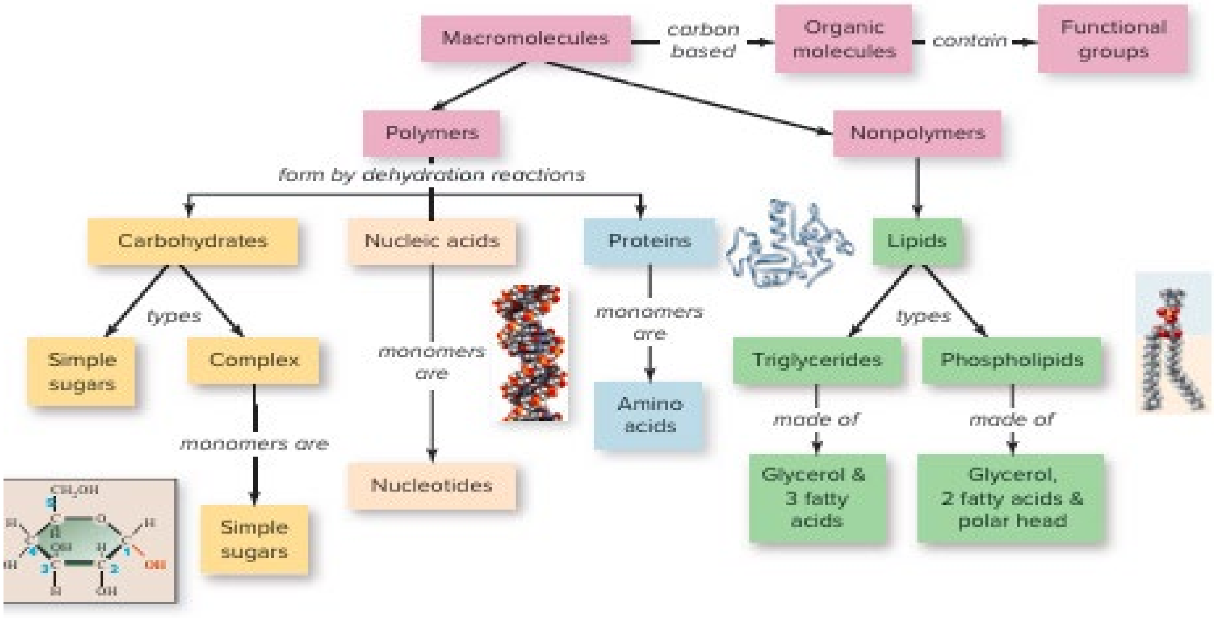
Major Classes: The four major classes of organic biomolecules are:

Carbohydrates
Lipids
Proteins
Nucleic Acids

Composition of a Cell

The following table illustrates the approximate chemical composition of a typical mammalian cell, highlighting the significance of these biomolecules:

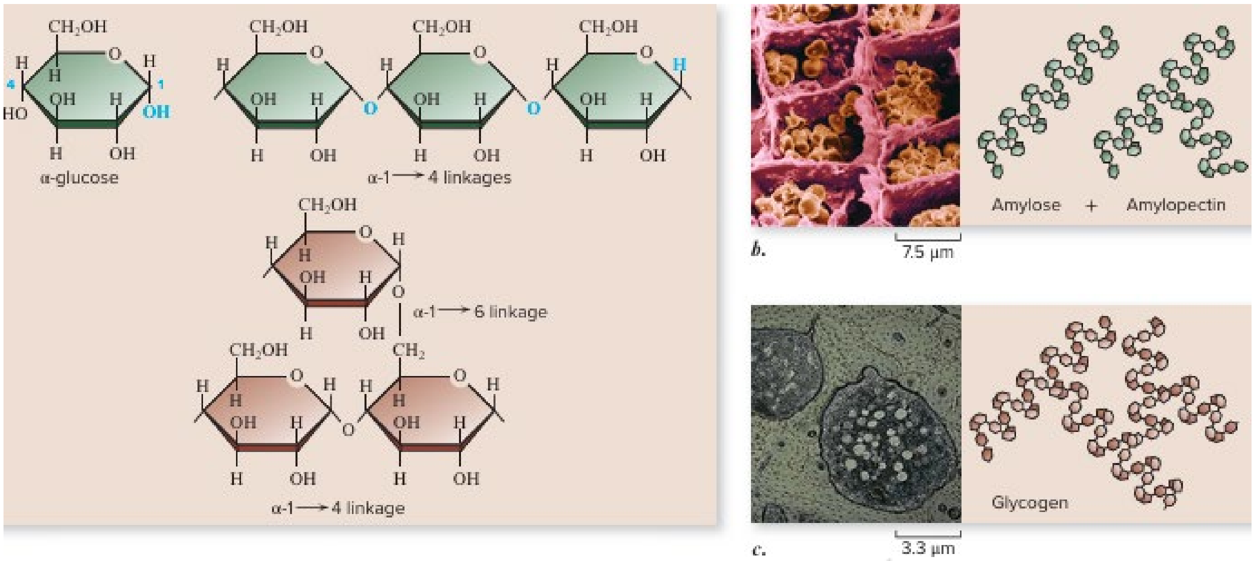
Chemical Component	Percentage in Mammalian Cell
Water	70%
Proteins	18%
Carbohydrates	4%
Lipids	3%
DNA	0.25%
RNA	1.1%
Other Organics & Ions	3.65%



A general sketch of Biopolymers

Carbohydrates

Definition: Carbohydrates are primarily defined as polyhydroxy aldehydes or ketones, or substances that yield these upon hydrolysis. They are commonly known as 'sugars' or 'saccharides'.



Homopolysaccharides: Composed of a single type of monosaccharide. Examples include starch, glycogen, cellulose, and chitin.

Heteropolysaccharides: Composed of two or more different types of monosaccharides. Examples include hyaluronic acid, heparin, and peptidoglycan.

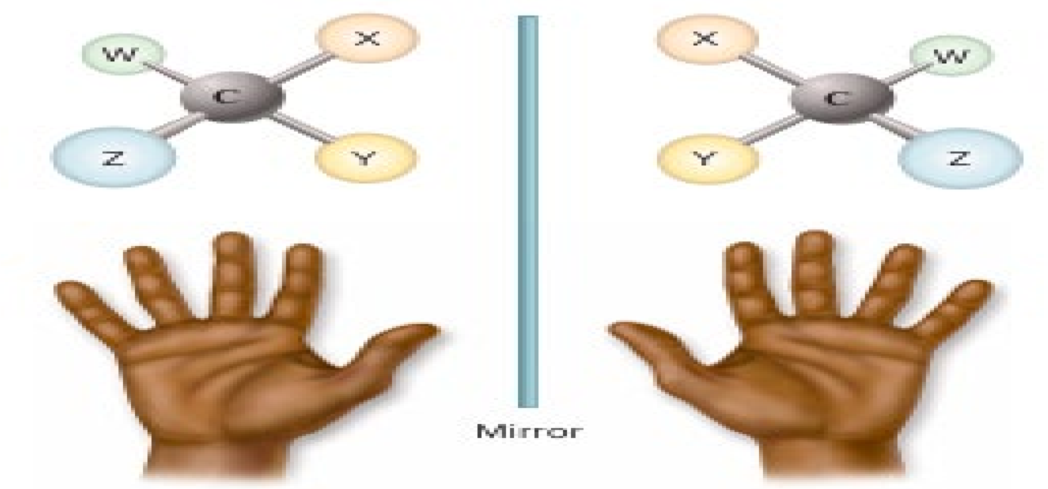
Monosaccharides: Structure and Stereochemistry

Basic Structure and Nomenclature

Monosaccharides are polyhydroxy aldehydes (aldoses) or polyhydroxy ketones (ketoses). The carbonyl carbon is designated C-1 for aldoses and is usually C-2 for ketoses. The number of carbon atoms in the chain is indicated by prefixes: triose (3C), tetrose (4C), pentose (5C), hexose (6C), and heptose (7C). These prefixes are combined with the functional group designation: aldotriose, ketopentose, aldohexose, etc. Monosaccharides with 5 or more carbon atoms predominantly exist in cyclic hemiacetal or hemiketal forms rather than as open-chain structures.

Stereochemistry and Fischer Projections

The carbon atoms in monosaccharides (**Carbonyl carbon and terminal –CH_2OH carbons are achiral**.) are chiral centers, leading to a multitude of stereoisomers. Emil Fischer's two-dimensional projection formulas provide a standardized way to represent the three-dimensional configuration of sugars. In a Fischer projection, the carbon chain is drawn vertically with the most oxidized carbon (the aldehyde or ketone) at or near the top. By convention, horizontal lines represent bonds projecting out of the plane of the paper (towards the viewer), and vertical lines represent bonds projecting behind the plane (away from the viewer).

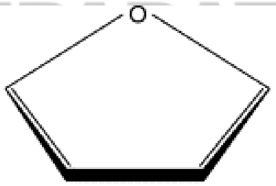


The **D and L system**

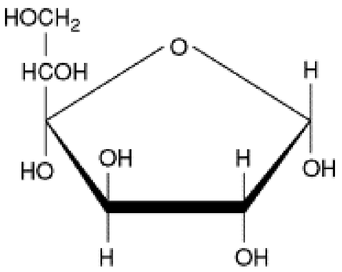
It classifies monosaccharides based on the configuration of the chiral carbon *farthest* from the carbonyl group (the penultimate carbon). When the sugar is drawn in a Fischer projection with the carbonyl group at the top, if the hydroxyl (–OH) group on this highest-numbered chiral carbon is on the *right*, the sugar is designated a **D-sugar**. If it is on the *left*, it is designated an **L-sugar**. The vast majority of naturally occurring sugars in metabolic pathways are of the D-configuration. It is critical to understand that the D/L designation is independent of the optical rotation (dextrorotatory [+] or levorotatory [–]) of the compound. For example, D-glucose is dextrorotatory, while D-fructose is strongly levorotatory.

Cyclic Structures: Hemiacetal and Hemiketal Formation

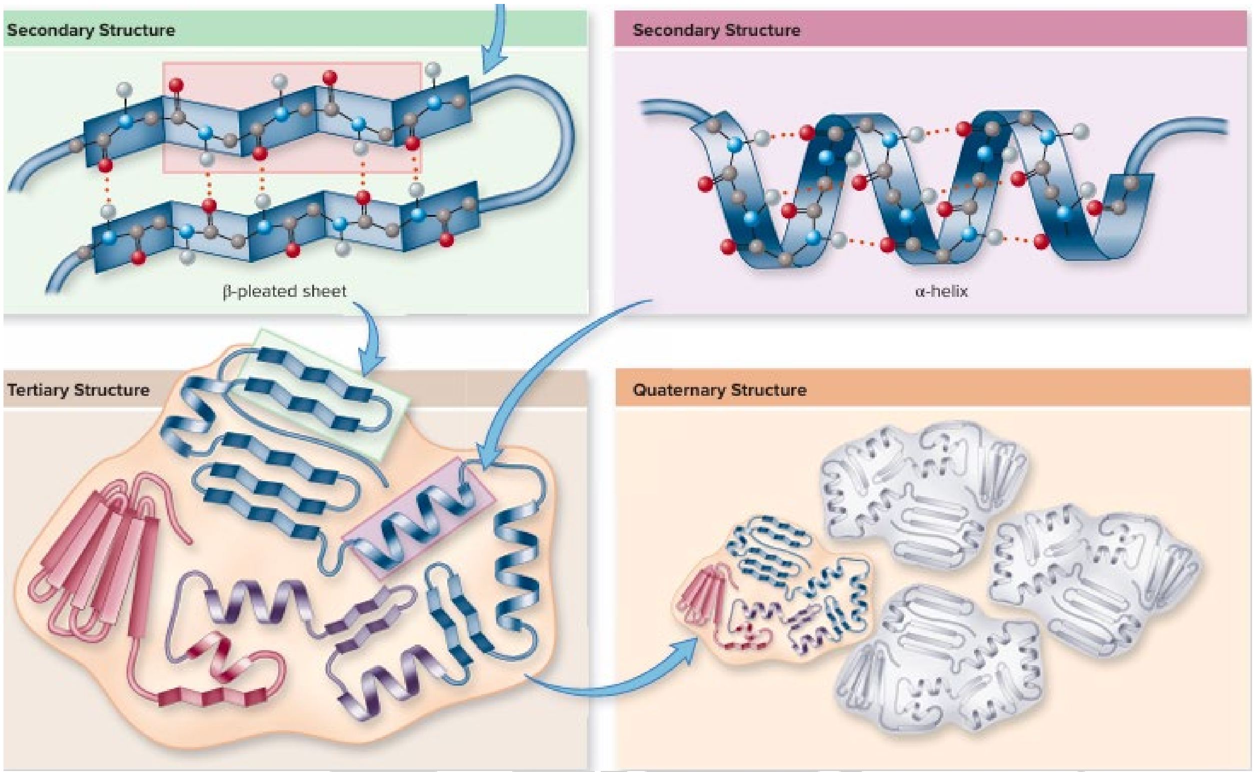
In aqueous solution, the open-chain form of a pentose or hexose is in equilibrium with cyclic forms. This cyclization occurs through an intramolecular nucleophilic addition reaction. The carbonyl group (C=O) reacts with a hydroxyl group (–OH) elsewhere in the same molecule to form a cyclic hemiacetal (from an aldose) or hemiketal (from a ketose). For aldoses, the hydroxyl group on C-5 is most commonly involved, attacking the carbonyl carbon (C-1) to form a six-membered ring called a **pyranose** (analogous to the compound pyran). Alternatively, attack by the hydroxyl on C-4 leads to a five-membered **furanose** ring (analogous to furan). Glucose, for instance, exists predominantly as glucopyranose.



Furan



α-D-Glucofuranose



Titration Curves and the Henderson-Hasselbalch Equation

Titration of an amino acid with a strong acid or base reveals its buffering regions and allows for the determination of its pK_a values. For a simple, neutral amino acid like alanine, the titration curve shows two distinct stages, corresponding to the sequential deprotonation of the two ionizable groups. The first buffer region (at low pH) corresponds to the carboxyl group (pK_{a1} =2.3). The second buffer region (at higher pH) corresponds to the amino group (pK_{a2} =9.7). For amino acids with ionizable side chains (e.g., aspartic acid, lysine, histidine), the titration curve has three stages.

The **Henderson-Hasselbalch equation**, $pH = pK_a + \log([A^-]/[HA])$, is used to relate the pH of a solution to the ratio of the concentrations of the protonated (HA) and deprotonated (A^-) forms of an acid group. It is instrumental in pI calculated from appropriate pK_a values and understanding the charge state of amino acids and proteins at any given pH.

For a neutral amino acid: $pI = (pK_{a1} + pK_{a2}) / 2$.

For an acidic amino acid For acidic amino acids: $pI = (pK_{a1} + pK_aR) / 2$, where pK_{a1} is the α-COOH and pK_aR is the side chain COOH

For basic amino acids: $pI = (pK_aR + pK_{a2}) / 2$, where pK_aR is the side chain and pK_{a2} is the α-NH_3^+

Electrophoresis

Electrophoresis is a powerful analytical technique that separates a mixture of amino acids or proteins based on their differential migration in an electric field at a given pH. The direction and rate of migration depend on the molecule's net charge. At a pH above its pI, an amino acid carries a net negative charge and migrates toward the anode (+). At a pH below its pI, it carries a net positive charge and migrates toward the cathode (–). At its pI, it does not migrate. By choosing an appropriate buffer pH, complex mixtures can be effectively separated.

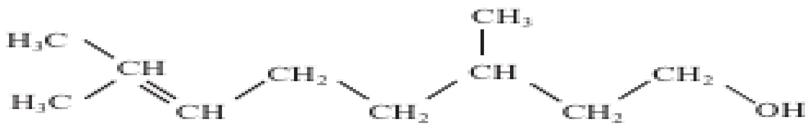
Triterpenoids (C_{30}): Six isoprene units. Squalene is first epoxidized to **2,3-oxidosqualene**, then cyclized by **oxidosqualene cyclase** to form lanosterol (in animals) or cycloartenol (in plants)., the precursor to all steroids in animals.

Tetraterpenoids (Carotenoids, C_{40}): Eight isoprene units. Examples: **β-Carotene** (orange pigment in carrots, precursor to vitamin A), **Lycopene** (red pigment in tomatoes), **Lutein**.

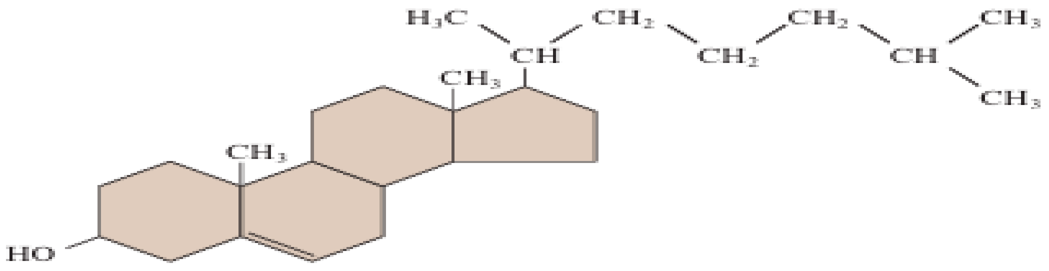
Polyterpenoids: Many isoprene units. Examples: Natural rubber (**cis-polyisoprene**), gutta-percha (**trans-polyisoprene**), **Dolichols** (carriers in glycoprotein synthesis).

Steroids

Steroids are lipids characterized by a specific fused-ring system: the **steroid nucleus** or **perhydrocyclopentanophenanthrene**. This consists of three six-membered cyclohexane rings (A, B, C) and one five-membered cyclopentane ring (D). Steroids are derived from the triterpene lanosterol.



a. Terpene (citronellol)



b. Steroid (cholesterol)

Cholesterol

Cholesterol is the **most abundant sterol in animal tissues**. It is a crucial component of animal cell membranes, modulating fluidity and permeability. It serves as the metabolic precursor for all other steroid hormones, bile acids, and vitamin D.

Structure: A hydroxyl group at C-3 (characteristic of sterols), a double bond between C-5 and C-6, and an 8-carbon branched hydrocarbon chain attached to C-17.

Transport: Being insoluble in blood, cholesterol is transported in lipoprotein particles (LDL, HDL).

Clinical Significance: High levels of LDL-cholesterol are associated with the formation of atherosclerotic plaques in arteries, leading to coronary artery disease and stroke.

Steroid Hormones

These are signaling molecules derived from cholesterol that act on nuclear receptors to regulate gene expression. They are classified by their source and function:

1. **Sex Hormones (Gonadal Steroids):**

Androgens (Male): Promote male secondary sexual characteristics. **Testosterone** is the primary androgen.

Estrogens (Female): Promote female secondary sexual characteristics and regulate the menstrual cycle. **Estradiol** is the most potent; note its aromatic A-ring.

Topic-Wise One-Liners on Biochemistry

1. Introduction to Biomolecules

1. **Biomolecules** are organic molecules essential for cellular structure, function, and metabolism.
2. The four major classes of organic biomolecules are **Carbohydrates, Lipids, Proteins, and Nucleic Acids**.
3. A typical mammalian cell is composed of approximately **70% water**.
4. After water, **proteins** are the most abundant chemical component in a mammalian cell (18%).
5. **Nucleic Acids (DNA & RNA)** together constitute about 1.35% of a mammalian cell's chemical composition.

2. Carbohydrates

6. **Carbohydrates** are defined as polyhydroxy aldehydes or ketones, or substances that yield them upon hydrolysis.
7. The general empirical formula for carbohydrates is **$C_x(H_2O)y$**.
8. The primary function of carbohydrates is to serve as a **primary energy source**, with glucose being the main fuel.
9. Carbohydrates are classified into **monosaccharides, oligosaccharides, and polysaccharides** based on the number of monosaccharide units.
10. **Monosaccharides** are the simplest sugars that cannot be hydrolyzed into smaller units.
11. Monosaccharides are classified based on the number of carbon atoms as **trioses, tetroses, pentoses, and hexoses**.
12. **Glucose** is an aldohexose with the molecular formula $C_6H_{12}O_6$ and is also known as dextrose or blood sugar.
13. In an aqueous solution, glucose predominantly exists in a cyclic form called **glucopyranose**.
14. The α and β forms of a sugar are called **anomers**, differing at the anomeric carbon.
15. **Mutarotation** is the spontaneous change in optical rotation of a sugar in solution due to interconversion between α and β anomers.
16. **Epimers** are monosaccharides that differ in configuration around a single carbon atom, other than the anomeric carbon (e.g., Glucose and Galactose at C4).
17. **Oligosaccharides** yield 2 to 10 monosaccharide units upon hydrolysis, with disaccharides being the most common.
18. Disaccharide units are joined by a **glycosidic bond**.
19. **Maltose** is a reducing sugar composed of two glucose units with an α-1,4 glycosidic linkage.
20. **Lactose**, or milk sugar, is a reducing sugar composed of galactose and glucose with a β-1,4 linkage.
21. **Sucrose** is a non-reducing sugar composed of glucose and fructose with an α,β-1,2 linkage and does not show mutarotation.
22. **Polysaccharides** are polymers of monosaccharides, are tasteless and amorphous, and are sparingly soluble in water.
23. **Starch**, a plant storage polysaccharide, is a polymer of α-D-glucose and is a mixture of amylose and amylopectin.
24. **Amylose** is an unbranched chain of glucose with α-1,4 linkages and gives a blue color with iodine.
25. **Amylopectin** is a branched chain of glucose with α-1,4 and α-1,6 linkages.
26. **Glycogen**, the animal storage polysaccharide, is more branched than amylopectin and gives a red color with iodine.
27. **Cellulose**, a structural polysaccharide in plants, is a linear polymer of β-D-glucose with β-1,4 linkages and is indigestible by humans.
28. **Inulin**, a polymer of fructose, is used to measure the **Glomerular Filtration Rate (GFR)**.
29. **Reducing sugars** have a free

Practice MCQs

Q1. Which of the following is the most abundant biomolecule on Earth?
A) Proteins
B) Lipids
C) Carbohydrates
D) Nucleic acids
Answer: Carbohydrates

Q2. The general formula Cx(H2O)y is characteristic of which class of biomolecules?
A) Proteins
B) Lipids
C) Carbohydrates
D) Nucleic acids
Answer: Carbohydrates

Q3. Which term describes compounds such as sucrose, lactose, and maltose?
A) Monosaccharides
B) Polysaccharides
C) Disaccharides
D) Trisaccharides
Answer: Disaccharides

Q4. Glucose and fructose are examples of:
A) Disaccharides
B) Polysaccharides
C) Oligosaccharides
D) Monosaccharides
Answer: Monosaccharides

Q5. Starch and cellulose are examples of:
A) Monosaccharides
B) Disaccharides
C) Polysaccharides
D) Trisaccharides
Answer: Polysaccharides

Q6. Carbohydrates that cannot be hydrolyzed into simpler sugars are called:
A) Oligosaccharides
B) Polysaccharides
C) Monosaccharides
D) Disaccharides
Answer: Monosaccharides

Q7. Sucrose on hydrolysis yields:
A) Glucose + Glucose
B) Glucose + Galactose
C) Glucose + Fructose
D) Fructose + Fructose
Answer: Glucose + Fructose

Q8. Lactose is a disaccharide found in milk and is composed of:
A) Glucose + Glucose
B) Glucose + Galactose
C) Glucose + Fructose
D) Galactose + Fructose
Answer: Glucose + Galactose

Q9. Which carbohydrate is known as "animal starch"?
A) Cellulose
B) Glycogen
C) Starch
D) Maltose
Answer: Glycogen

Q10. The structural polysaccharide in plants is:
A) Starch
B) Glycogen
C) Cellulose
D) Chitin
Answer: Cellulose

Q11. Which of the following is a reducing sugar?
A) Sucrose
B) Lactose
C) Trehalose
D) Cellobiose
Answer: Both Lactose and cellobiose

Q12. Benedict's reagent is used to test for:
A) Proteins
B) Lipids
C) Reducing sugars
D) Non-reducing sugars
Answer: Reducing sugars

Q13. The cyclic hemiacetal forms of glucose are called:
A) Glycosides
B) Anomers
C) Epimers
D) Enantiomers
Answer: Anomers

Q14. The change in optical rotation of a sugar solution until an equilibrium is reached is called:
A) Epimerization
B) Mutarotation
C) Inversion

Industrial Chemistry & Synthetic Polymers

Introduction to Industrial Chemistry

Definition: Industrial chemistry is the branch of chemistry concerned with the chemical processing of raw materials into usable and profitable products. Industrial chemistry involves chemical processes at commercial scale (tonnage quantities) converting raw materials into products with economic value, including final consumer goods or intermediate chemicals.

Scope and Importance:

It is a highly diverse manufacturing sector that produces thousands of chemicals, which the public encounters as end-use products.

These products are valued for the specific effects or properties they provide, such as non-stick coatings or weed killers.

Chemical processing involves both chemical conversion (e.g., manufacturing sulphuric acid from sulphur) and physical operations (e.g., heat transfer, temperature control) to achieve high yields required by a competitive industry.

Importance of Chemical Industry in Pakistan's Economy

The chemical industry is a cornerstone of Pakistan's economic development and international trade.

Economic Contribution: It accounts for approximately **4.5% of total exports** and **12% of total imports**.

Industrial Role: It is a key enabler for **forward-oriented industries** (e.g., automobiles, textiles, leather goods, food and beverages) and **backward-oriented industries** (e.g., supplying surfactants to oil refineries).

Growth Factors: The sector has experienced rapid growth due to:

Rising domestic demand

Improved availability of raw materials

Supportive government policies

Increased foreign investment

Technological advancements

Enhanced regional integration

Raw Materials for Chemical Industries in Pakistan

Pakistan is endowed with a variety of raw materials that fuel its chemical sector.

A. Fossil Fuels & Minerals:

Coal, Natural Gas, and Oil

Salt, Limestone, Sulphur

Specialized minerals like Phosphates and Fluorides

Other mineral deposits: Copper, Gold, Chromite, Bauxite

Key Industrial Raw Materials:

Soapstone: A primary raw material; 85% is used in textiles, paper, soap, detergents, leather, and food industries.

Polyvinyl Chloride (PVC): Mainly used for producing pipes, fittings, cables, profiles, and footwear. Driven largely by the construction industry (70% of consumption). Also used in medical devices and packaging.

Polyesters:

Its Acid Hydrolysis Produces diol and dicarboxylic acid.

Its Alkaline Hydrolysis Produces diol and carboxylate salt.

Polyamides:

Its Acid Hydrolysis will Produces dicarboxylic acid and amine salt.

Its Alkaline Hydrolysis will Produces dicarboxylate salt and diamine.

Solutions for Recycling and Biodegradable Polymers

Recycling: The best solution. Plastics are identified by resin codes (e.g., 1-PET, 2-HDPE, 3-V, 4-LDPE, 5-PP, 6-PS), then shredded, washed, and melted for reuse.

Biodegradable Polymers: Designed to be broken down by microorganisms.

Examples: Polyglycolic Acid (PGA), Polylactic Acid (PLA), Polyhydroxybutyrate (PHB).

Use: PGA-PLA copolymers are used to make absorbable surgical sutures.

Key Differences between Polymerization Types

Feature	**Addition Polymerization**	**Condensation Polymerization**
Monomers	Unsaturated (e.g., alkenes)	Bifunctional (e.g., diol + diacid, diamine + diacid)
By-Product	None	Small molecule (e.g., H_2O, HCl, NH_3)
Growth Mechanism	Chain reaction (initiation, propagation, termination)	Stepwise reaction
Polymer Formula	Same as monomer's empirical formula	Different from monomer's empirical formula
Rate of Reaction	Fast	Slow
Molecular Mass	Increases rapidly	Increases slowly
Examples	Polyethene, PVC, Polystyrene	Nylon, Polyester, Polyurethane

Most Exam-Tested Polymers at a Glance

Polymer	**Monomer(s)**	**Polymerization Type**	**Key Property**	**Major Application**
LDPE	Ethylene	Free radical addition	Flexible, branched	Bags, films
HDPE	Ethylene	Coordination (Z-N/Phillips)	Rigid, linear	Bottles, pipes
PP	Propylene	Coordination (Z-N)	High Tm, stiff	Packaging, automotive
PVC	Vinyl chloride	Free radical addition	Versatile (rigid/flexible)	Pipes, profiles, medical

106. **Bakelite structure:** Cross-linked 3D network; rigid, heat resistant, electrically insulating.
107. **Bakelite applications:** Electrical switches, pot handles, billiard balls, antique jewelry.
108. **Melamine-Formaldehyde:** Hard, scratch-resistant; dinnerware, laminates (Formica®).
109. **Urea-Formaldehyde:** Adhesives (particleboard), electrical fittings.
110. **Epoxy Resins:** Epichlorohydrin + bisphenol A; cured with amines or anhydrides.
111. **Epoxy properties:** Excellent adhesion, chemical resistance, mechanical strength.
112. **Epoxy applications:** Adhesives (Araldite®), coatings, composites (carbon fiber), electronics (circuit boards), flooring.

SECTION 19: ADDITIONAL ENGINEERING POLYMERS

113. **Polycarbonate (PC):** Bisphenol A + phosgene (or diphenyl carbonate); transparent, impact resistant.
114. **PC applications:** Safety glasses, bulletproof glass, CDs/DVDs, automotive headlamps, electronics.
115. **PMMA (Polymethyl methacrylate, Plexiglas®, Perspex®):** Transparent alternative to glass; lightweight; lenses, signage.
116. **POM (Polyoxymethylene, Acetal, Delrin®):** High stiffness, low friction; gears, bearings, zippers.
117. **ABS (Acrylonitrile Butadiene Styrene):** Graft copolymer; tough, impact resistant; automotive parts, LEGO® bricks, electronics housings.
118. **PEEK (Polyether ether ketone):** High-performance engineering thermoplastic; medical implants, aerospace.

SECTION 20: POLYMER IDENTIFICATION (RECYCLING CODES)

Code	Abbreviation	Full Name	Common Applications
1	PETE or PET	Polyethylene Terephthalate	Beverage bottles, food containers
2	HDPE	High-Density Polyethylene	Milk jugs, detergent bottles, pipes
3	V or PVC	Polyvinyl Chloride	Pipes, window frames, medical tubing
4	LDPE	Low-Density Polyethylene	Plastic bags, squeeze bottles, films
5	PP	Polypropylene	Food containers, bottle caps, automotive
6	PS	Polystyrene	Disposable cups, packaging, insulation
7	OTHER	Other (PC, ABS, Nylon, etc.)	Multi-layer, specialty plastics

SECTION 21: INDUSTRIAL CHEMICAL PROCESSES

119. **Haber process:** $N_2 + 3H_2 \rightleftharpoons 2NH_3$; Fe catalyst, 200-250 atm, 400-450°C.
120. **Contact Process:** $2SO_2 + O_2 \rightleftharpoons 2SO_3$; V_2O_5 catalyst; for H_2SO_4 production.
121. **Solvay process:** $2NaCl + CaCO_3 \rightarrow Na_2CO_3$ (soda ash) $+ CaCl_2$; ammonia recovery.
122. **Down's Process:** Electrolysis of molten NaCl (with $CaCl_2$) for Na metal.
123. **Hall-Héroult Process:** Electrolysis of Al_2O_3 in molten cryolite for Al metal.
124. **Frasch Process:** Mining sulfur using superheated water (170°C) + compressed air.
125. **Bosch Process:** Historical H_2 production; $C + H_2O \rightarrow CO + H_2$; $CO + H_2O \rightarrow CO_2 + H_2$.
126. **Steam Reforming:** $CH_4 + H_2O \rightarrow CO + 3H_2$ (for H_2 production).

2	HDPE	High-Density Polyethylene	Milk jugs, detergent bottles, pipes
3	V or PVC	Polyvinyl Chloride	Pipes, window frames, medical tubing
4	LDPE	Low-Density Polyethylene	Plastic bags, squeeze bottles, films
5	PP	Polypropylene	Food containers, bottle caps, automotive
6	PS	Polystyrene	Disposable cups, packaging, insulation
7	OTHER	Other (PC, ABS, Nylon, etc.)	Multi-layer, specialty plastics

Practice MCQs

1. Which type of polymerization involves the elimination of a small molecule like water or methanol?

A) Addition polymerization
B) Chain-growth polymerization
C) Condensation polymerization
D) Free-radical polymerization

Answer: Condensation polymerization

2. What is the main component used in the production of soda ash (sodium carbonate) via the Solvay process?

A) NaCl
B) $CaCO_3$
C) $NaHCO_3$
D) NH_3

Answer: NaCl

3. Which catalyst is used in the Ziegler-Natta polymerization of propylene?

A) BF_3/H_2O
B) $TiCl_4 + Al(C_2H_5)_3$
C) Butyllithium
D) Benzoyl peroxide

Answer: $TiCl_4 + Al(C_2H_5)_3$

4. What is the primary raw material for the production of PVC?

A) Ethylene
B) Acetylene
C) Vinyl chloride
D) Propylene

Answer: Vinyl chloride

5. Which type of copolymer has long blocks of one monomer alternating with blocks of another?

A) Random copolymer
B) Alternating copolymer
C) Block copolymer
D) Graft copolymer

Answer: Block copolymer

6. What is the repeating unit in polyvinyl acetate (PVA)?

A) $–CH_2–CHCl–$
B) $–CH_2–CH(OCOCH_3)–$
C) $–CH_2–CH(C_6H_5)–$
D) $–CH_2–CH(CN)–$

Answer: $–CH_2–CH(OCOCH_3)–$

7. Which of the following is a thermosetting polymer?

A) Polyethylene
B) Polystyrene
C) Bakelite
D) PVC

Answer: Bakelite

8. What is the main use of epoxy resins?

A) Food packaging
B) Adhesives and coatings
C) Plastic bottles

Surface Chemistry

Introduction of Surface chemistry

Surface chemistry is the branch of chemistry concerned with the phenomena occurring at the interfaces between distinct phases, such as between a solid and a gas, a solid and a liquid, or two immiscible liquids. This interface is a region where the properties of matter differ significantly from those in the bulk phases, creating a unique environment crucial for a variety of physical, chemical, and biological processes. The behavior of molecules at surfaces governs processes like heterogeneous catalysis, where reactions are accelerated on solid surfaces; corrosion, the degradation of materials through surface reactions; adhesion and lubrication, critical in material science and engineering; membrane function in biology; and separation techniques such as chromatography and froth flotation.

The historical development of surface chemistry

Is started with the work of pioneers like **Irving Langmuir**, who formulated fundamental theories of adsorption and surface films, **and J. Willard Gibbs**, whose thermodynamic treatment of surfaces laid the groundwork for understanding surface tension and adsorption.

Some key terms

Adsorption is the accumulation of molecules (gases, liquids, or dissolved solids) on the surface of another substance (adsorbent) through physical or chemical forces. It is a surface phenomenon, meaning the

Occlusion Occlusion is the absorption of gases into the bulk of a solid metal by occupying interstitial spaces in the crystal lattice" (e.g., hydrogen in Pd). For example, Activated charcoal adsorbs odour-causing molecules from the air. Silica gel adsorbs moisture from the surroundings to prevent spoilage. Ink particles are adsorbed onto paper fibers. Different molecules adsorb to varying degrees on a stationary phase, facilitating their separation.

Desorption: This is the release of adsorbed molecules from the surface of the adsorbent. It can be achieved by increasing temperature, reducing pressure, or introducing a competing adsorbate.

Sorption: This is a broader term encompassing both adsorption (accumulation on the surface) and absorption (penetration throughout the bulk). For example, a sponge sorbs water, both by adsorption on its surface and by absorption within its pores

Catalysis

Catalysis is a process wherein a substance known as a catalyst alters the rate of a chemical reaction without itself undergoing a net chemical change or being consumed in the overall reaction. The term was coined by the Swedish chemist **Jöns Jakob Berzelius** in 1836, deriving from the Greek words *kata* (wholly) and *lein* (to loosen), reflecting the early idea that a catalyst "loosened" the bonds within reactants. A catalyst provides an **alternative reaction** pathway with a lower activation energy, thereby increasing the frequency of successful molecular collisions. It is paramount to understand that a catalyst does not affect the thermodynamic equilibrium of a reversible reaction; it only hastens the rate at which equilibrium is attained. According to the **principle of microscopic reversibility**.

Catalyst

that accelerates the forward reaction must equally accelerate the reverse reaction. Catalysts are highly specific; a substance that catalyzes one reaction may have no effect on another, and different catalysts can steer the same reactants toward entirely different products. Catalysis is over 90% of all chemical

Test / Property	Emulsion	Gel
Basic Nature	Liquid dispersed in another liquid (liquid–liquid colloid)	Liquid dispersed in a solid network (semi-solid colloid)
Dilution Test	Can be diluted only with the dispersion medium (O/W with water, W/O with oil)	Cannot be diluted easily; structure breaks on dilution
Dye Test	Dye soluble in dispersion medium spreads uniformly in continuous phase	Dye does not spread uniformly; remains localized
Electrical Conductivity	O/W emulsions conduct electricity; W/O conduct poorly	Generally poor conductivity
Filter Paper Test	Produces a wet/liquid ring on filter paper	Does not spread readily; little or no ring
Microscopic View	Shows distinct droplets of one liquid in another	Shows continuous solid network with trapped liquid
Flow Behavior	Flows like a viscous liquid	Semi-solid; does not flow easily
Effect of Heating	May separate into two liquid layers (emulsion breaks) **Bancroft's rule**: The phase in which emulsifier is more soluble becomes continuous phase"	Shows syneresis (liquid oozes out) instead of layer separation
Stability Mechanism	Stabilized by emulsifying agent	Stabilized by 3-D solid network structure
Common Examples	Milk, mayonnaise, vanishing cream	Jelly, silica gel, gelatin gel

Difference between Emulsion and Gel — Identification Tests

Applications of Colloids

Colloids are integral to daily life and industry:

Food Industry: Milk, butter, cheese, ice cream, bread, jellies, mayonnaise.

Medicines: Colloidal drugs for better absorption (e.g., colloidal silver, milk of magnesia), emulsions (cod liver oil), and ointments.

Water Purification: Coagulation of negatively charged colloidal impurities using alum [$Al_2(SO_4)_3$] or ferric sulfate, which form positively charged $Al(OH)_3$ or $Fe(OH)_3$ flocs that entrap impurities.

Smoke Precipitation (Cottrell Precipitator): Smoke (solid-in-gas colloid) is passed through a high-voltage electrostatic field. Particles become charged and are attracted to oppositely charged electrodes, where they are collected. Used in thermal power plants and cement factories to control air pollution.

Artificial Kidney (Dialysis): Mimics the natural function of kidneys by removing waste products (urea, uric acid) from blood using a semipermeable membrane, while retaining essential colloidal proteins and blood cells.

Delta Formation: When river water (containing negatively charged colloidal clay particles) meets sea water (rich in electrolytes like Na^+, Mg^{2+}, Ca^{2+}), coagulation occurs, leading to the deposition of sediment and the formation of deltas.

Paints, Inks, and Lubricants: Paints are colloidal dispersions of pigments; printing inks are often sols; lubricating greases are colloidal gels.

- **Froth Flotation:** In ore dressing, the process of separating sulfide ores from gangue relies on the selective adsorption of collectors (like xanthates) on mineral surfaces, making them hydrophobic so they attach to air bubbles.
- **Chromatography:** All chromatographic techniques (TLC, HPLC, GC) are based on differential adsorption/desorption of components between a stationary phase (adsorbent) and a mobile phase.
- **Dyeing:** Adsorption of dyes on fabrics.

Ion-Exchange Adsorption

This is a special type of chemisorption where ions from an electrolyte solution are exchanged with similarly charged ions present on the surface of an insoluble solid—the **ion-exchange resin**. These are synthetic organic polymers with a cross-linked structure and bearing functional groups.

- **Cation Exchange Resins:** Contain acidic groups like $-SO_3^-H^+$ or $-COO^-H^+$. H^+ form used in deionization; Na^+ form used in softening. for other cations (e.g., Na^+, Ca^{2+}, Mg^{2+}). $R-SO_3^-H^+ + Na^+ \rightleftharpoons R-SO_3^-Na^+ + H^+$.
- **Anion Exchange Resins:** Contain basic groups like $-N^+(CH_3)_3OH^-$ or $-NH_3^+OH^-$. They exchange their OH^- ions for other anions (e.g., Cl^-, SO_4^{2-}). $R-N^+(CH_3)_3OH^- + Cl^- \rightleftharpoons R-N^+(CH_3)_3Cl^- + OH^-$.

Applications:

- **Water Softening:** Hard water (containing Ca^{2+}, Mg^{2+}) is passed through a column of cation exchange resin (in Na^+ form). Ca^{2+}/Mg^{2+} replace Na^+ on the resin, producing soft water.
- **Deionization/Demineralization of Water:** Water is passed sequentially through a cation exchange resin (H^+ form) and an anion exchange resin (OH^- form). All cations are replaced by H^+ and all anions by OH^-, which combine to form pure H_2O.
- **Medical Applications:** Removing excess Na^+ from the body in edema, reducing stomach acidity.
- **Separation and Purification:** Used in metallurgy, sugar refining, and hydrometallurgy.

Topic Wise One Liners: Surface Chemistry

CATALYSIS

1. **Catalysis** is the process where a **catalyst** changes the rate of a reaction without being consumed.
2. **Jöns Jakob Berzelius** coined the term "catalysis" and introduced the concept.
3. A catalyst may **increase** (positive catalyst) or **decrease** (negative catalyst) the reaction rate.
4. **Homogeneous catalysis** occurs when the catalyst and reactants are in the same phase.
5. **Heterogeneous catalysis** involves a catalyst in a different phase from the reactants.
6. **Enzyme catalysis** refers to biological catalysts that are protein molecules.
7. A catalyst remains **unchanged in mass and chemical composition** after the reaction.
8. A **small quantity** of catalyst can produce a large amount of product.
9. Finely divided catalysts are **more effective** due to larger surface area.
10. Catalysts are **specific**—a catalyst for one reaction may not work for another.
11. A catalyst **cannot initiate** a reaction but can accelerate an existing one.
12. Catalysts do **not alter** the equilibrium constant or position of equilibrium.
13. Catalysts **lower the activation energy** of a reaction.
14. **Promoters** are substances that enhance catalyst activity (e.g., Mo for Fe in Haber process).
15. **Catalytic Poisoning** are impurities that reduce or destroy catalyst activity (e.g., As_2O_3 for Pt).
16. **Autocatalysis** occurs when a reaction product acts as its own catalyst (e.g., acetic acid in ester hydrolysis).

Practice MCQs

1. Which chemist coined the term “catalysis”?
A) Robert Boyle
B) Antoine Lavoisier
C) Jöns Jakob Berzelius
D) Dmitri Mendeleev
Answer: Jöns Jakob Berzelius

2. A catalyst remains ______ at the end of the reaction.
A) Chemically changed
B) Consumed
C) Unchanged in mass and composition
D) Reduced in mass
Answer: Unchanged in mass and composition

3. In homogeneous catalysis, the catalyst and reactants are in:
A) Different phases
B) Same phase
C) Solid state only
D) Gaseous state only
Answer: Same phase

4. Which is an example of heterogeneous catalysis?
A) Hydrolysis of sugar with acid
B) Oxidation of SO_2 with NO
C) Haber process with Fe catalyst
D) Inversion of cane sugar with invertase
Answer: Haber process with Fe catalyst

5. Enzymes are:
A) Carbohydrates
B) Lipids
C) Proteins
D) Nucleic acids
Answer: Proteins

6. A substance that enhances catalyst activity is called a:
A) Poison
B) Promoter
C) Inhibitor
D) Solvent
Answer: Promoter

7. Arsenic oxide (As_2O_3) acts as a poison for which catalyst?
A) Fe in Haber process
B) Pt in Contact process
C) Ni in hydrogenation
D) V_2O_5 in oxidation
Answer: Pt in Contact process

8. Autocatalysis is observed in the hydrolysis of:
A) Sucrose
B) Ethyl acetate
C) Starch
D) Protein
Answer: Ethyl acetate

9. Negative catalysis is also known as:
A) Promotion
B) Inhibition
C) Autoacceleration
D) Poisoning
Answer: Inhibition

10. A catalyst works by:
A) Increasing activation energy
B) Lowering activation energy
C) Changing equilibrium constant
D) Increasing product yield
Answer: Lowering activation energy

11. The theory that explains homogeneous catalysis via intermediate compound formation is called:
A) Adsorption theory
B) Collision theory
C) Intermediate compound theory
D) Transition state theory
Answer: Intermediate compound theory

12. Active centres on a catalyst are:
A) Inactive sites
B) Sites with high catalytic activity
C) Poisoned sites

Environmental Chemistry

Introduction

Environmental chemistry is a specialized discipline concerned with the origin, transport, reactions, effects, and ultimate fate of chemical species within the natural environment. A particular focus is placed on pollutants, which are substances introduced into the environment as a result of human activity, leading to deleterious effects on ecosystems, human health, and the built environment. This field is fundamentally interdisciplinary, synthesizing principles and methodologies from core sciences such as chemistry and biology, and applied fields including physics, medicine, agriculture, public health, and various engineering disciplines. Its practical remit encompasses the analysis, understanding, and mitigation of pressing global challenges, including atmospheric and aquatic pollution, hazardous waste management, soil degradation, and the depletion of natural resources. The study is not merely descriptive but analytical, seeking to understand the complex chemical interactions that govern the behavior of pollutants across different environmental compartment

Components of the Environment

The environment is conceptually divided into four principal, interconnected spheres or geochemical reservoirs: the atmosphere, hydrosphere, lithosphere, and biosphere. This compartmentalization provides a framework for studying the distribution and cycling of elements and compounds.

(i) Atmosphere

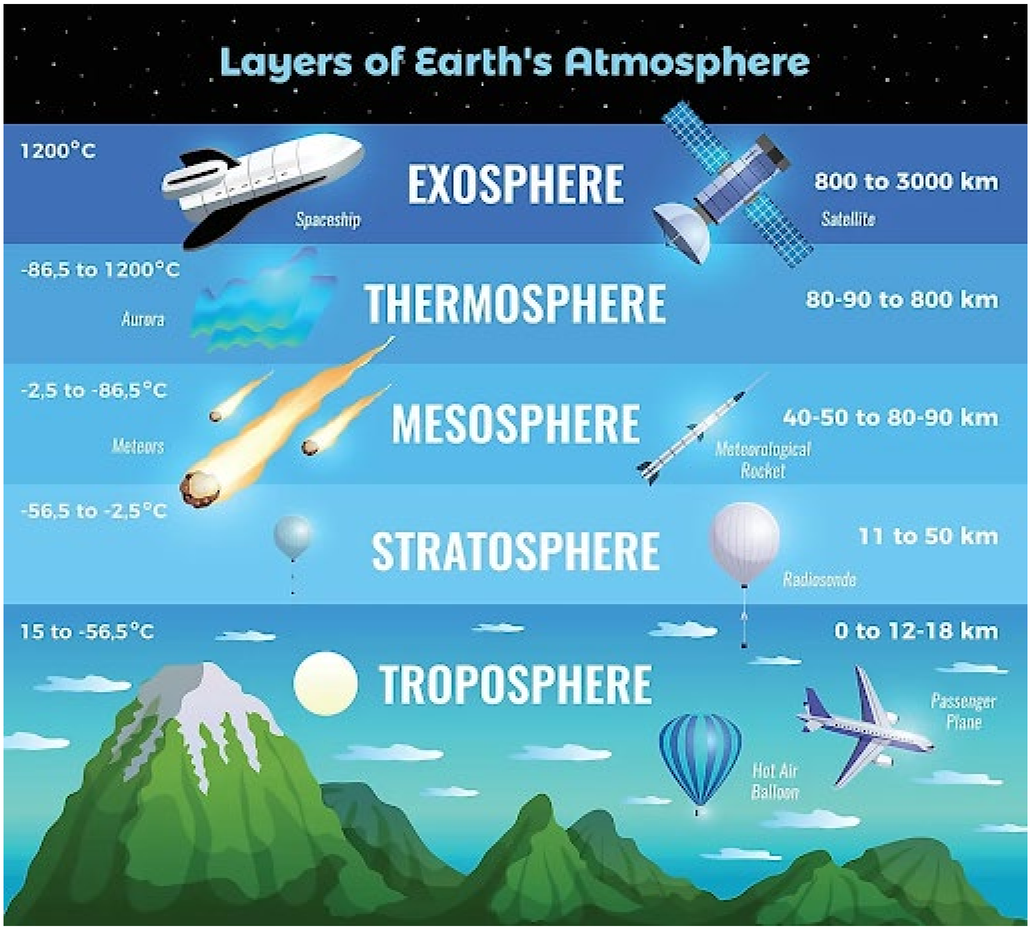
The atmosphere is the gaseous envelope surrounding the Earth, retained by gravitational attraction. It is not a uniform layer but is stratified based on thermal characteristics. Its total vertical extent is approximately 1000 kilometers from the Earth's surface, though about half of its total mass is concentrated within the lowest 5.6 kilometers, a region known as the troposphere where most weather phenomena occur.

The composition of dry air, by volume, is remarkably constant in the lower atmosphere: molecular nitrogen (N_2) constitutes about 78%, molecular oxygen (O_2) about 21%, and argon (Ar) about 0.93%. Carbon dioxide (CO_2), a critical greenhouse gas, is present at a much lower concentration of approximately 0.041% (or 410 parts per million), though this value is rising due to anthropogenic activities. Trace gases include neon (Ne), helium (He), methane (CH_4), krypton (Kr), hydrogen (H_2), nitrous oxide (N_2O), and xenon (Xe). Importantly, the atmosphere also contains a highly variable amount of water vapor (H_2O), typically ranging from 1% to 4% by volume, which is crucial for the hydrological cycle and climate regulation.

The atmosphere performs several vital functions. It acts as a protective shield, absorbing a significant portion of the sun's harmful ultraviolet (UV) radiation—primarily in the stratospheric ozone layer—and cosmic rays. This absorption is essential for protecting terrestrial life from ionizing and mutagenic radiation. Furthermore, the atmosphere is the primary reservoir for gases necessary for life: oxygen for aerobic respiration in animals and most microorganisms, and carbon dioxide for photosynthesis in plants, algae, and cyanobacteria. Nitrogen, though inert in its molecular form, is utilized by specialized nitrogen-fixing bacteria and archaea, entering the biosphere through biological and industrial nitrogen fixation processes. Finally, the atmosphere plays a central role in regulating the Earth's energy balance through the greenhouse effect, whereby certain gases trap infrared radiation emitted from the Earth's surface, maintaining a global average temperature suitable for liquid water and life.

(ii) Hydrosphere

through an ecosystem via food chains and webs, starting with primary producers (photosynthesizers), moving to consumers (herbivores, carnivores), and ending with decomposers (bacteria, fungi) that break down organic matter, releasing nutrients back into the abiotic environment. Any substance introduced into an ecosystem that adversely affects the health of organisms, the quality of life, or the natural functioning of ecological processes is defined as a pollutant. The rapid expansion of human population, urbanization, industrialization, and intensive agriculture over the past century has dramatically increased the quantity and diversity of pollutants entering the environment, posing significant challenges to ecological integrity and public health.

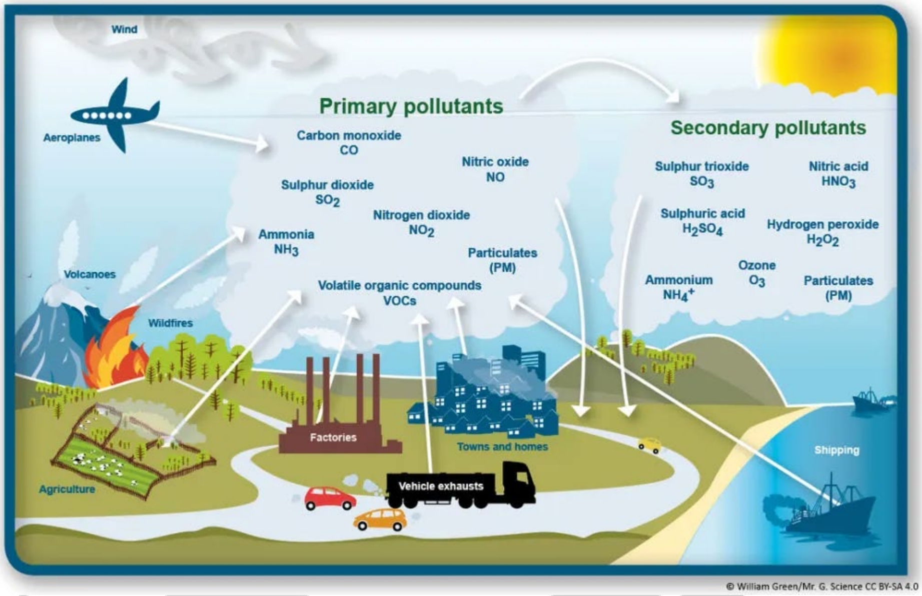


Air Pollution

Air pollution occurs when the concentration of certain substances in the atmosphere reaches levels that are harmful to living organisms, damage materials, or cause nuisance. These substances, known as air pollutants, can be gases, liquid droplets, or solid particles. They are classified based on their origin.

Carbon Monoxide (CO):

Carbon monoxide is a product of incomplete combustion, where insufficient oxygen is present to fully oxidize carbon to carbon dioxide (CO_2). Its natural sources are relatively minor and include volcanic eruptions, natural gas seeps, and atmospheric oxidation of methane. The overwhelming majority of CO emissions are anthropogenic, with the transportation sector—particularly gasoline and diesel-powered



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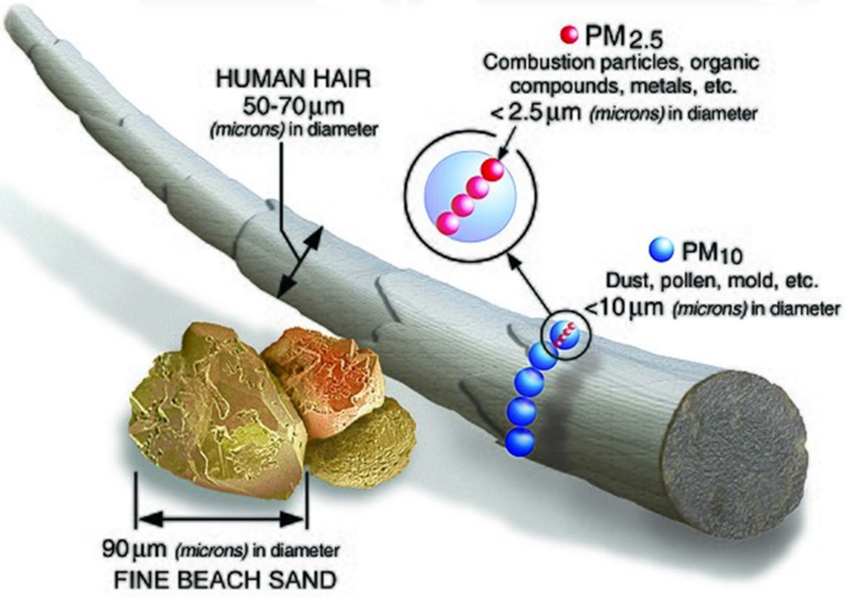
Particulate Matter (PM):
Types: Viable (pollen, spores) and non-viable (dust, soot).
Effects: Respiratory and cardiovascular diseases, reduced visibility, environmental damage.

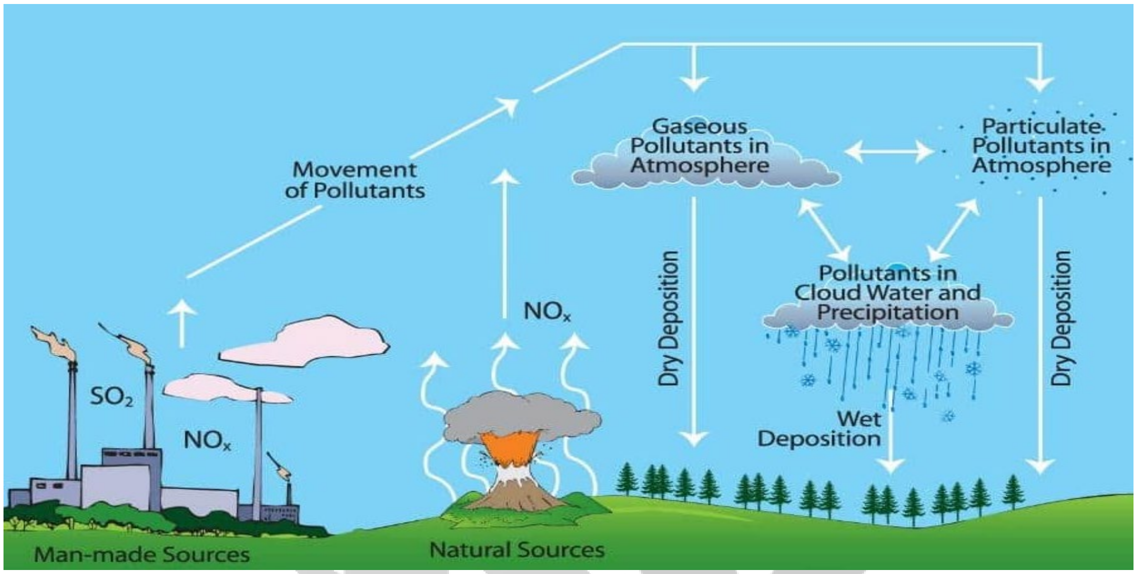


Harms of particulates

Respiratory Problems: Fine particulate matter can penetrate deep into the lungs, causing or worsening conditions like asthma, bronchitis, and chronic obstructive pulmonary disease (COPD).

Cardiovascular Diseases: Long-term exposure to particulate pollution can increase the risk of heart attacks, strokes, and other cardiovascular problems due to inflammation and damage to blood vessels.

Materials and Structures: Acids react with calcium carbonate in building materials like limestone, marble, and mortar, causing erosion, pitting, and loss of structural detail on statues and historical monuments. Metals (e.g., steel, bronze) corrode more rapidly in an acidic environment. Paints and automotive coatings can be degraded.



Smog

Smog, a portmanteau of "smoke" and "fog," describes a visible air pollution phenomenon. There are two chemically distinct types.

Classical (Reducing) Smog (London-type): This is primarily an issue of coal-burning cities in temperate climates. Its main chemical constituents are sulfur dioxide (SO_2) and particulates (soot, fly ash). It is called "reducing" because it is characterized by high concentrations of reducing agents (SO_2, soot). It forms under cool, humid, and stagnant atmospheric conditions, typically in winter. The infamous London smog of 1952, which caused thousands of deaths, is a classic example. Health effects are primarily due to respiratory irritation from SO_2 and particulates.

Photochemical (Oxidizing) Smog (Los Angeles-type): This is the characteristic brown haze of modern, sunny, automobile-dominated cities. It is not a product of coal burning but of vehicular emissions. Its formation requires three key ingredients: sunlight, high concentrations of nitrogen oxides (NO_x), and volatile organic compounds (VOCs). The chemistry is a complex set of chain reactions initiated by sunlight. A simplified sequence begins with the photolysis of nitrogen dioxide, which produces an oxygen atom that reacts with O_2 to form ozone:

$NO_2(g) + h\nu$ (sunlight) $\rightarrow NO(g) + O(g)$

$O(g) + O_2(g) + M \rightarrow O_3(g) + M$ (where M is a third body that absorbs excess energy)

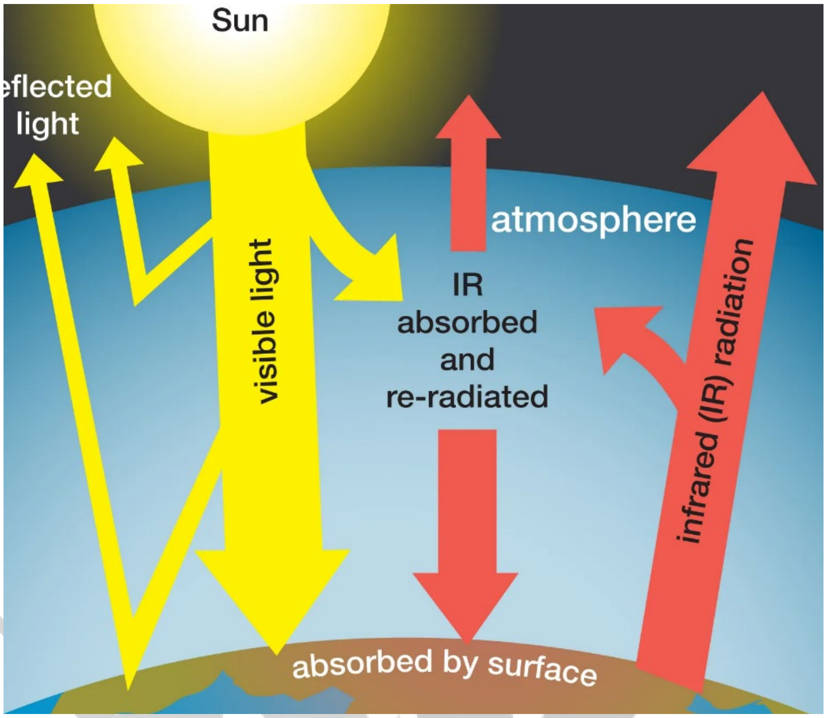
However, the freshly formed ozone quickly reacts with nitric oxide to reform NO_2 and O_2:

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

In the absence of VOCs, this cycle would reach a steady state with low ozone levels. VOCs break this cycle. They react with hydroxyl radicals (•OH) and other oxidants to form organic peroxy radicals ($RO_2•$). These radicals efficiently oxidize NO to NO_2 **without consuming ozone:**

$RO_2• + NO \rightarrow RO• + NO_2$

This uncoupled reaction allows ozone to accumulate, as NO is converted to NO_2 without being



Water Pollution

Water pollution is the contamination of water bodies (e.g., lakes, rivers, oceans, aquifers) by substances harmful to the organisms that depend on them or that make the water unfit for its intended uses (drinking, recreation, irrigation). Pollutants can be point sources (discharged from a single, identifiable location like a pipe) or non-point sources (diffuse runoff from agricultural land or urban areas).

Sources and Effects of Water Pollution:

1. Livestock Waste: Manure from concentrated animal feeding operations (CAFOs) is a major non-point source pollutant. When improperly managed, it runs off into surface waters or leaches into groundwater. It introduces high levels of **nutrients** (nitrogen and phosphorus), which cause eutrophication; **organic matter**, which increases biochemical oxygen demand (BOD), depleting dissolved oxygen; and **pathogens** (bacteria like *E. coli*, viruses, parasites) that cause waterborne diseases such as dysentery, typhoid, cholera, and giardiasis.

2. Oil Spills: Accidental releases of crude oil or refined products from tankers, pipelines, offshore platforms, or land-based facilities have catastrophic effects on marine and coastal ecosystems. The toxic components of oil (especially light aromatic hydrocarbons like benzene, toluene, xylene) can poison marine life, from plankton to fish and birds. The physical coating of animals with oil destroys the insulating properties of fur and feathers, leading to hypothermia and death. Oil slicks block sunlight, reducing photosynthesis in phytoplankton and sea grasses. Long-term ecological damage includes disruption of reproductive cycles, tainting of fisheries, and persistence of heavy oil components in sediments.

3. Detergents: While modern detergents are largely biodegradable, they still pose environmental threats. Phosphates, once common as "builders" in detergents to soften water, are potent fertilizers that accelerate eutrophication. Surfactants (the cleaning agents) can be toxic to aquatic life, especially in their untreated state, by damaging gill membranes in fish. Furthermore, certain surfactants can mobilize (solubilize) toxic

Regulation of agricultural runoff.
Oil spill management techniques.
Public awareness and legislation.
Soil Pollution Control
Bioremediation.
Proper waste disposal.
Reduced use of chemical pesticides and fertilizers.

Environmental Chemistry - Topic-wise One-Liners

1. Introduction to Environmental Chemistry

1. **Environmental chemistry** studies chemical species, their sources, reactions, transport, effects, and fates in the environment.
2. It focuses on **pollutants from human activities** and their adverse impacts on ecosystems, health, and quality of life.
3. It is **interdisciplinary**, integrating principles from biology, physics, medicine, agriculture, public health, and engineering.
4. It addresses real-world issues like **pollution, waste management, and resource conservation**.

2. Components of the Environment

5. The environment comprises four main **spheres**: Atmosphere, Hydrosphere, Lithosphere, and Biosphere/Ecosphere.
6. The **atmosphere** is the gaseous layer extending up to about **1000 km** around the Earth.
7. Atmospheric composition: **N_2 (78%), O_2 (21%), Ar (0.9%), CO_2 (0.03%)**, with trace gases.
8. Half of the atmosphere's mass lies within the lower **5.6 km**.
9. The **hydrosphere** includes all water bodies: oceans, rivers, lakes, glaciers, ice caps, and groundwater.
10. Global water distribution: **Oceans 97%** (saline), **Glaciers and ice caps 2%**, **Freshwater 1%**.
11. Freshwater usage: **Agriculture (69%), Industry (23%), Domestic (8%)**.
12. The **lithosphere** is Earth's rigid rocky crust extending to **100 km** depth.
13. The lithosphere's mass is composed of approximately **8 elements**; O (46.6%), Si (27.7%), and Al (8.1%) are the top three.
14. The **biosphere/ecosphere** is the region where life exists, interacting with other spheres.
15. An **ecosystem** is a smaller, functional unit of the **biosphere**.
16. A **pollutant** is any substance that adversely affects health, quality of life, or ecosystem function.

3. Types of Pollution & Pollutants

17. **Pollution** is the introduction of harmful substances into the environment causing negative effects.
18. Pollutants can be **natural** (volcanic ash) or **man-made** (chemicals, plastics, industrial waste).
19. Pollutants can be **physical, chemical, or biological**.
20. Pollution is classified as **atmospheric, water, soil, noise, and light pollution**.
21. **Noise** is considered a **non-physical and non-chemical pollutant**.

4. Air Pollution

22. **Air pollution** is the introduction of harmful substances into the atmosphere.
23. **Primary pollutants** are emitted directly from sources (e.g., CO, SO_2, NO_x, VOCs, particulate matter).
24. **Secondary pollutants** form via chemical reactions in the atmosphere (e.g., H_2SO_4, HNO_3, O_3, PBN and PAN).

Practice MCQs

1. **Which component of the environment contains the highest proportion of nitrogen by volume?**
A) Biosphere
B) Lithosphere
C) Hydrosphere
D) Atmosphere
Answer: Atmosphere

2. **What is the approximate thickness of the Earth's atmosphere above the surface?**
A) 500 km
B) 1000 km
C) 1500 km
D) 2000 km
Answer: 1000 km

3. **Which layer of the atmosphere contains the ozone layer?**
A) Troposphere
B) Stratosphere
C) Mesosphere
D) Thermosphere
Answer: Stratosphere

4. **What percentage of Earth's total water supply is available as fresh water?**
A) 1%
B) 2%
C) 3%
D) 4%
Answer: 1%

5. **Which of the following is not a primary pollutant?**
A) Carbon monoxide
B) Sulphur dioxide
C) Ozone
D) Nitrogen oxides
Answer: Ozone

6. **What is the largest natural source of sulphur dioxide in the atmosphere?**
A) Volcanic eruptions
B) Forest fires
C) Bacterial action
D) Lightning
Answer: Volcanic eruptions

7. **Which gas is produced by incomplete combustion of carbonaceous compounds?**
A) CO_2
B) SO_2
C) CO
D) NO
Answer: CO

8. **What is the primary human activity source of carbon monoxide?**
A) Agriculture
B) Deforestation
C) Transportation
D) Volcanic activity
Answer: Transportation

9. **Nitrogen dioxide (NO_2) is primarily produced by the reaction of nitric oxide with which substance?**
A) Water
B) Oxygen
C) Carbon dioxide
D) Sulphur dioxide
Answer: Oxygen

10. **Which of the following is a secondary pollutant formed in the atmosphere?**
A) Carbon monoxide
B) Sulphur dioxide
C) Peroxyacetyl nitrate (PAN)
D) Methane
Answer: Peroxyacetyl nitrate (PAN)

11. **What is the pH of unpolluted rainwater?**
A) 5.6
B) 6.5
C) 7.0
D) 8.0
Answer: 5.6

12. **Acid rain with a pH below 5 is primarily due to the presence of which acids?**

Radio and Nuclear Chemistry

Introduction to Radioactivity

Radioactivity is defined as the spontaneous disintegration of an unstable atomic nucleus, accompanied by the emission of penetrating radiation such as alpha particles, beta particles, and gamma rays. This process is independent of external factors such as temperature, pressure, or chemical combination and depends solely on the internal instability of the nucleus. **Radioactive elements** are those whose nuclei are unstable and undergo spontaneous decay to achieve a more stable configuration. Examples include Uranium (U), Radium (Ra), Polonium (Po), and Thorium (Th).

The historical background of radioactivity begins with **Wilhelm Roentgen's** discovery of X-rays in 1895, which are high-energy electromagnetic waves. This sparked interest in "invisible rays." In 1896, **Henri Becquerel** accidentally discovered that uranium salts emitted invisible, penetrating rays capable of darkening a photographic plate without any external energy source; this was the first observation of natural radioactivity. In 1898, **Marie and Pierre Curie** coined the term "radioactivity" and discovered two new, highly radioactive elements: Polonium and Radium. Finally, in 1899, **Ernest Rutherford** identified and named the three types of radiation based on their penetrating power and charge: **Alpha (α), Beta (β), and Gamma (γ)**. These discoveries fundamentally changed the understanding of the atom, revealing that it was not indivisible and that the nucleus could undergo transformations.

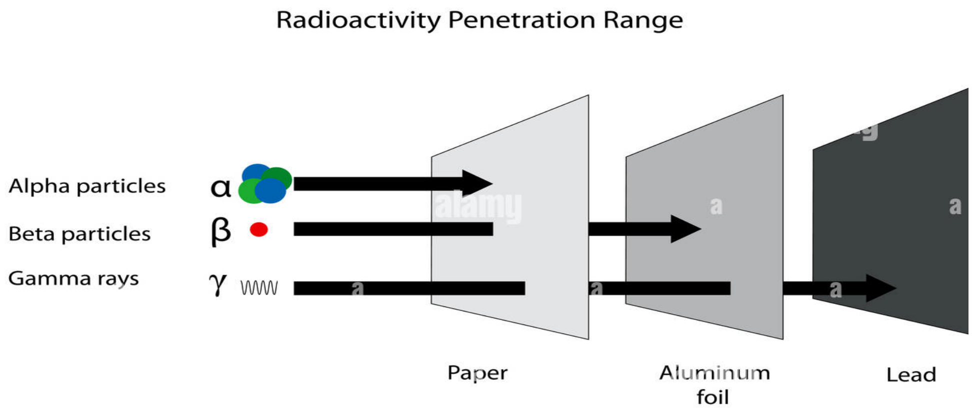
Types and Properties of Radiations

Rutherford's experiment of passing radiation through an electric field allowed classification based on their deflection. The properties of the three main types of radiation are distinct and critical to understanding their behavior and applications.

Alpha (α) Rays consist of streams of helium nuclei ($^{4}_{2}He^{2+}$). They carry a charge of +2 and have a mass of approximately 4 atomic mass units (amu). Alpha particle speed depends on kinetic energy; typically a **few % to 10% of c** (order of magnitude).". Due to their high mass and charge, they possess very high ionizing power but very low penetrating power; they can be stopped by a sheet of paper, skin, or a few centimeters of air. In an electric or magnetic field, alpha particles are deflected toward the negative plate.

Beta (β) Rays are streams of fast-moving electrons . They carry a charge of -1 and have a negligible mass (about 1/1837 amu). Their velocity can reach up to 90% of the speed of light. Beta penetration is **moderate**; stopped by a few mm of Al/plastic; range in air is **energy-dependent**. Their ionizing power is moderate, roughly one-hundredth that of alpha particles. In an electric field, they are deflected toward the positive plate.

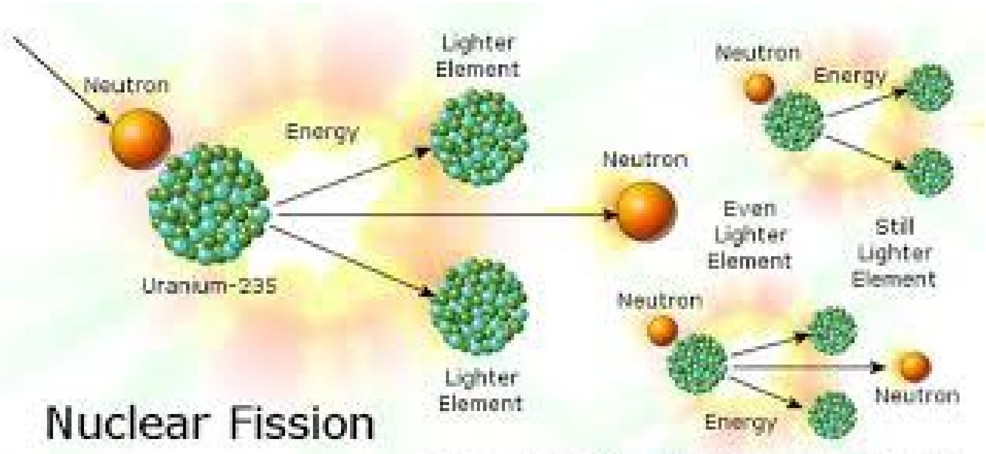
Gamma (γ) Rays are high-energy electromagnetic radiation (photons). They are neutral, massless, and travel at the speed of light. Gamma rays have very high penetrating power, requiring thick lead or concrete shielding to attenuate them. Their ionizing power is very low, making them weak ionizers. They are not deflected by electric or magnetic fields.



Key comparative points to remember are: The order of **ionizing power** is **α > β >** γ, and the order of **penetrating power** is **α < β <** γ.

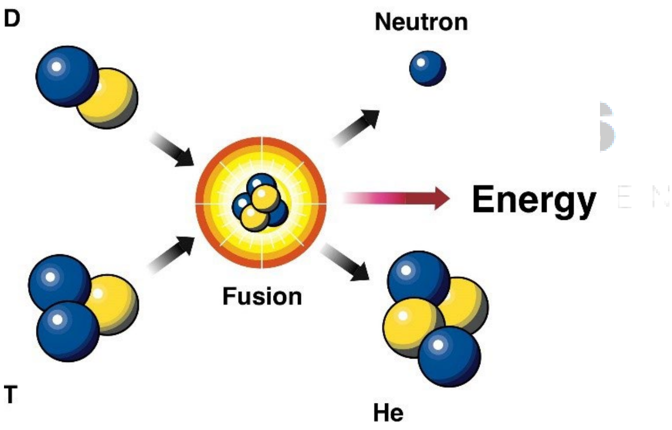
Property	**Alpha (α) Rays**	**Beta (β) Rays**	**Gamma (γ) Rays**
Nature & Identity	Streams of Helium nuclei	Streams of fast-moving electrons (Beta-minus (β^-) rays are streams of fast-moving electrons; beta-plus (β^+) rays are streams of positrons)	High-energy electromagnetic radiation (photons)
Charge	+2	-1	0 (Neutral)
Mass	4 amu (approx.)	1/1837 amu (negligible)	0 (massless)
Velocity	1/10th of speed of light	90% the speed of light **Exact is (0.3 to 0.99c)**	Speed of light
Penetrating Power	Very Low (stopped by paper, skin, or a few cm of air)	Moderate (stopped by a few mm of Aluminum or 1m of air)	Very High (requires thick lead or concrete to attenuate)
Ionizing Power	Very High (intense ionizers due to high mass and charge)	Moderate (about 1/100th of that of α-particles)	Very Low (weak ionizers)

Nuclear Fusion



Nuclear Fusion is the process in which two or more light atomic nuclei combine to form a single, heavier nucleus, releasing an enormous amount of energy. This process requires extremely high temperatures (millions of degrees Celsius) to overcome the electrostatic repulsion between the positively charged nuclei, hence it is termed a **thermonuclear reaction**. At these temperatures, matter exists in the plasma state.

The Sun's energy is produced primarily by the proton-proton chain (99%) with a small contribution from the CNO cycle (1%). For more massive stars, the CNO cycle dominates. A **Hydrogen Bomb (H-Bomb)** is an uncontrolled fusion device that uses a fission bomb as a trigger to achieve the necessary temperature and pressure for fusion of hydrogen isotopes like deuterium and tritium.



Fusion as a Future Energy Source Deuterium is abundant, **but tritium (required for D-T fusion**) is radioactive with a 12.3-year half-life and must be bred from lithium in the reactor blanket, higher energy yield per gram, and less long-lived radioactive waste compared to fission. However, major challenges remain in achieving and confining plasma at the required temperatures and pressures.

Artificial Radioactivity and Nuclear Isomerism

Artificial (Induced) Radioactivity refers to the phenomenon where stable nuclei are transformed into radioactive isotopes by bombarding them with high-energy particles like protons, neutrons, or alpha

Rayleigh-Jeans law, The Rayleigh-Jeans law accurately predicted black-body radiation at long wavelengths **but failed catastrophically** at short wavelengths (ultraviolet catastrophe), predicting infinite energy density. a problem known as the **ultraviolet catastrophe**. **Max Planck** resolved this in 1900 by proposing that energy is quantized, existing only in discrete amounts given by $E = nh\nu$, where n is an integer and h is Planck's constant. This led to the Planck distribution formula.

The **Photoelectric Effect**, where electrons are ejected from a metal surface by light, also defied classical explanation. Key observations were that ejection occurred only above a threshold frequency, and the kinetic energy of ejected electrons depended on frequency, not intensity.

Albert Einstein explained this in 1905 by proposing that light consists of particles called **photons**, each with energy **hν**. The kinetic energy of an ejected electron is given by $\frac{1}{2}m_e v^2 = h\nu - \Phi$, where Φ is the work function of the metal.

Wave-Particle Duality emerged as a central concept. **Louis de Broglie** hypothesized that particles could exhibit wave-like properties, with a wavelength given by $\lambda = h / p$, where p is momentum. The **Davisson-Germer experiment**, which demonstrated electron diffraction, confirmed the wave nature of particles.

In quantum mechanics, the state of a system is described by a **wavefunction, ψ**. The **time-independent Schrödinger equation** is the fundamental equation: $-\hbar^2/2m \, (d^2\psi/dx^2) + V(x)\psi = E\psi$, where V(x) is the potential energy, and E is the total energy.

According to the **Born Interpretation**, the square of the wave function's modulus, $|\psi|^2$, represents the **probability density** of finding a particle at a given point. The wavefunction itself is the probability amplitude.

The **Heisenberg Uncertainty Principle**, formulated by Werner Heisenberg, states that certain pairs of complementary observables, like position (x) and momentum (p_x), cannot be measured simultaneously with arbitrary precision: $\Delta x \, \Delta p_x \geq \hbar/2$.

Topic-Wise One-Liner: Radio and Nuclear Chemistry

Introduction to Radioactivity

1. **Radioactivity** is the spontaneous disintegration of unstable atomic nuclei, accompanied by the emission of penetrating radiation.
2. The radioactive decay process is independent of external factors like temperature, pressure, or chemical bonding.
3. **Radioactive elements**, such as Uranium, Radium, Polonium, and Thorium, possess unstable nuclei that decay to achieve a more stable configuration.

Historical Background

4. **Wilhelm Roentgen** discovered **X-rays** in 1895, sparking interest in "invisible rays."
5. **Henri Becquerel** accidentally discovered **natural radioactivity** from uranium salts in 1896.
6. **Marie and Pierre Curie** coined the term "radioactivity" and discovered the elements **Polonium** and **Radium** in 1898.
7. **Ernest Rutherford** identified and named **Alpha (α), Beta (β), and Gamma (γ)** radiations in 1899.

Types and Properties of Radiations

8. **Alpha particles** are helium nuclei ($^4_2He^{2+}$) with a charge of +2 and a mass of approximately 4 amu.
9. **Beta particles** are fast-moving electrons ($^0_{-1}e$) with a charge of -1 and negligible mass.

Practice MCQs

1. What is the defining characteristic of radioactivity?
A) It requires high temperature to initiate
B) It involves the spontaneous disintegration of unstable nuclei
C) It only occurs in man-made elements
D) It is highly dependent on chemical bonding
Answer: It involves the spontaneous disintegration of unstable nuclei

2. Who accidentally discovered natural radioactivity?
A) Marie Curie
B) Wilhelm Roentgen
C) Henri Becquerel
D) Ernest Rutherford
Answer: Henri Becquerel

3. Which scientists coined the term "radioactivity"?
A) Marie and Pierre Curie
B) Henri Becquerel
C) Ernest Rutherford
D) Wilhelm Roentgen
Answer: Marie and Pierre Curie

4. What is the identity of an alpha particle?
A) A high-energy electron
B) A helium nucleus
C) A high-energy photon
D) A proton
Answer: A helium nucleus

5. Which type of radiation has the highest penetrating power?
A) Alpha rays
B) Beta rays
C) Gamma rays
D) X-rays
Answer: Gamma rays

6. Which type of radiation has the highest ionizing power?
A) Alpha rays
B) Beta rays
C) Gamma rays
D) Neutrons
Answer: Alpha rays

7. In an electric field, towards which plate are beta particles deflected?
A) Negative plate
B) Positive plate
C) They are not deflected
D) Perpendicular to the field
Answer: Positive plate

8. Which instrument uses a supersaturated vapor to make radiation paths visible?
A) Geiger-Muller Counter
B) Scintillation Counter
C) Cloud Chamber
D) Ionisation Chamber
Answer: Cloud Chamber

9. What is the principle behind a Film Badge used for radiation monitoring?
A) Gas ionization
B) Light scintillation
C) Film darkening
D) Electron avalanche
Answer: Film darkening

10. The rate of radioactive disintegration is proportional to:
A) The decay constant only
B) The time elapsed
C) The number of undecayed atoms present
D) The half-life of the substance
Answer: The number of undecayed atoms present

11. The mathematical expression for the radioactive decay law is:
A) $N = N_0 / t$
B) $N = N_0 \lambda t$
C) $N = N_0 e^{(-\lambda t)}$

Basic Concepts of Organic Chemistry

Introduction to Organic Chemistry

Definition: Organic chemistry is the branch of chemistry that deals with the study of hydrocarbons (compounds of carbon and hydrogen) and their derivatives.

Historical Context: Initially, organic compounds were defined as those obtained from living organisms (plants and animals), based on the "Vital Force Theory." This theory was disproved by Friedrich Wöhler in 1828 when he synthesized urea (an organic compound) from ammonium cyanate (an inorganic salt). This landmark experiment paved the way for modern organic chemistry, which is based on the structure and reactivity of carbon compounds.

Unique Properties of Carbon

The existence of millions of organic compounds is attributed to the unique properties of the carbon atom:

Catenation: The unique ability of carbon atoms to form stable covalent bonds with other carbon atoms, leading to long chains (straight or branched) and rings of various sizes.

Tetravalency: A carbon atom has four valence electrons, allowing it to form four strong covalent bonds.

Formation of Multiple Bonds: Carbon can form stable double (C=C) and triple (C≡C) bonds with itself and other elements like oxygen and nitrogen.

Isomerism: Carbon compounds extensively exhibit isomerism, where different compounds can share the same molecular formula.

Classification of Organic Compounds

Organic compounds are broadly classified based on the arrangement of carbon atoms.

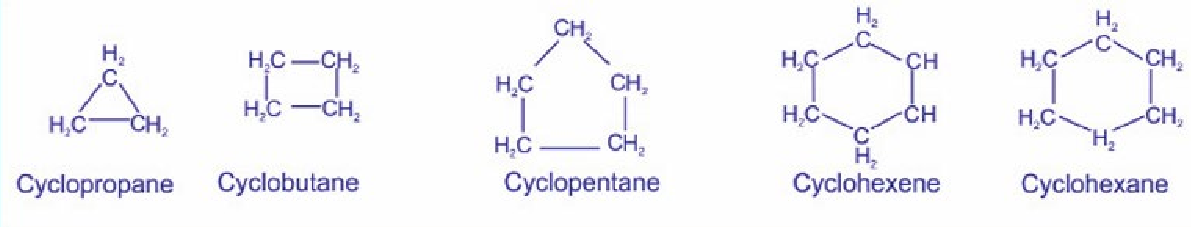
Acyclic or Open-Chain Compounds:

These compounds contain open chains of carbon atoms. The chains can be straight or branched.

Example: CH_3-CH_2-CH_2-CH_3 (n-Butane), CH_3-$CH(CH_3)$-CH_3 (Isobutane).

Cyclic or Closed-Chain Compounds:

These compounds contain one or more closed rings of atoms.

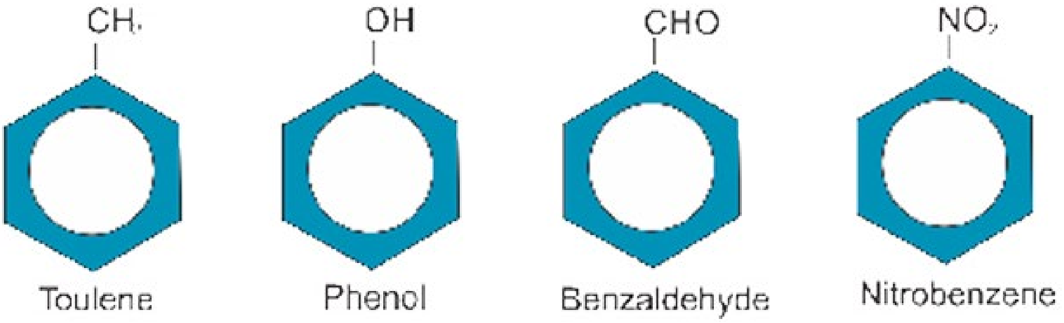


Cyclopropane Cyclobutane Cyclopentane Cyclohexene Cyclohexane

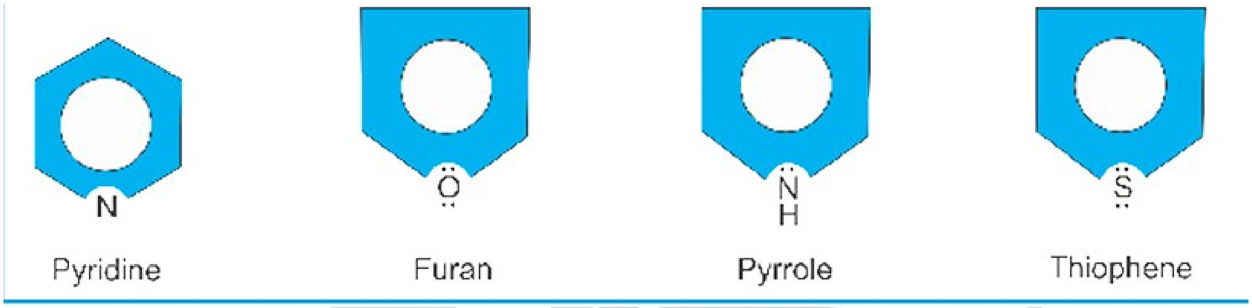
Homocyclic or Carbocyclic: The ring consists of only carbon atoms.

Alicyclic: Ring compounds resembling aliphatic compounds in their properties. (e.g., Cyclohexane).

Aromatic: Aromatic compounds are cyclic, planar, and contain a conjugated system with (4n+2) π electrons. Benzene is the classic example." (e.g., Benzene, Toluene).



Heterocyclic: The ring contains at least one atom other than carbon (a heteroatom like O, N, S).
Example: Pyridine, Furan, Thiophene.



Functional Groups

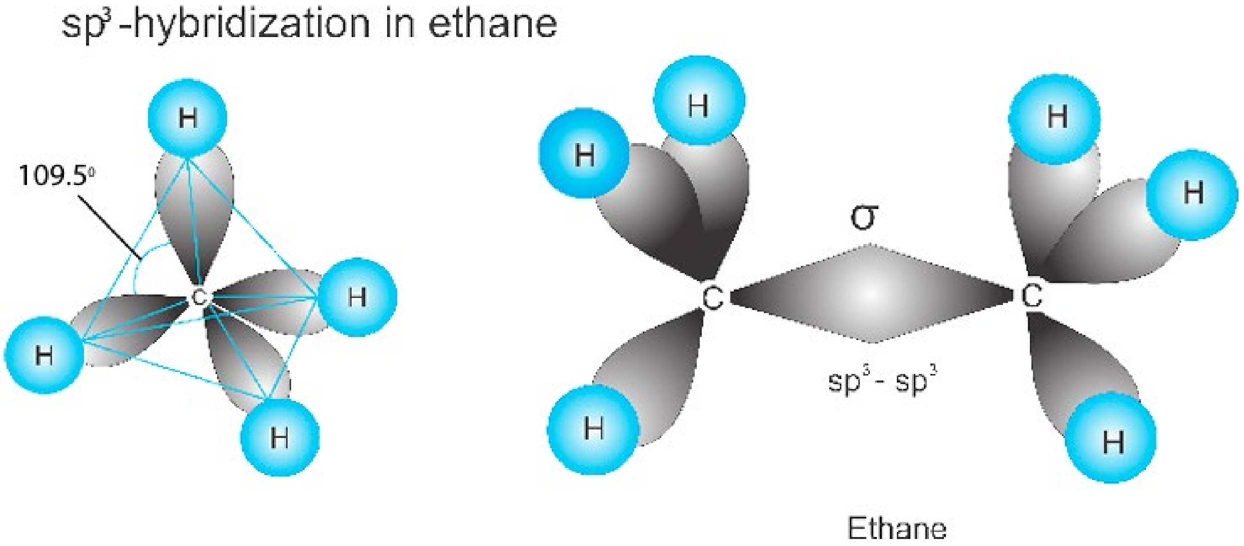
A functional group is an atom or a group of atoms within a molecule that determines its characteristic chemical reactions and largely dictates its physical properties.

Functional Group	Formula	Class of Compound	Example
Halo	-X (F, Cl, Br, I)	Alkyl Halide	CH_3-Cl (Chloromethane)
Hydroxyl	-OH	Alcohol	CH_3-CH_2-OH (Ethanol)
Carbonyl	-C=O	Aldehyde/Ketone	CH_3-CHO (Ethanal), CH_3-CO-CH_3 (Propanone)
Carboxyl	-COOH	Carboxylic Acid	CH_3-COOH (Ethanoic acid)
Alkoxy	-O-	Ether	CH_3-O-CH_3 (Methoxymethane)
Amino	-NH_2	Amine	CH_3-NH_2 (Methylamine)
Nitro	-NO_2	Nitro Compound	C_6H_5-NO_2 (Nitrobenzene)
Cyano	-C≡N	Nitrile	CH_3-C≡N (Ethanenitrile)

Hybridization And Molecular Shapes

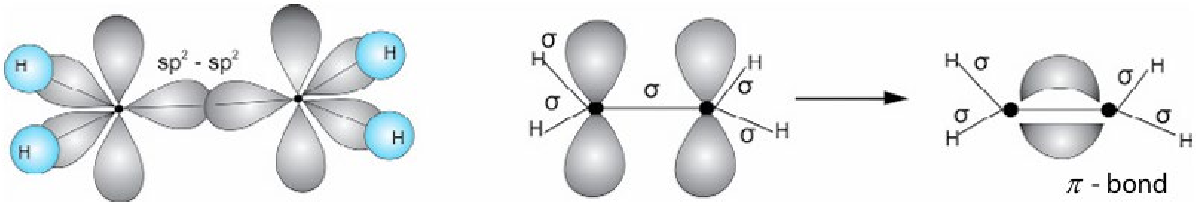
The concept of orbital hybridization, introduced by Linus Pauling, provides a powerful model for reconciling the tetravalency of carbon with the geometries observed in its compounds. Hybridization is a theoretical construct wherein atomic orbitals (s and p) from the same atom combine (mix) to form an equal number of new, degenerate (equal energy) hybrid orbitals. These hybrid orbitals have different shapes and directional properties from the original atomic orbitals and are better suited for forming strong, directional covalent bonds that satisfy the Valence Shell Electron Pair Repulsion (VSEPR) theory. VSEPR theory posits that electron pairs (both bonding and lone pairs) around a central atom will arrange themselves in three-dimensional space to be as far apart as possible to minimize electrostatic repulsion.

sp^3 Hybridization: This occurs when one 's' orbital and three p orbitals hybridize to form four equivalent sp^3 hybrid orbitals. These four orbitals are arranged in a tetrahedral geometry around the nucleus, with bond angles of approximately 109.5°. This geometry perfectly explains the structure of saturated carbon atoms.

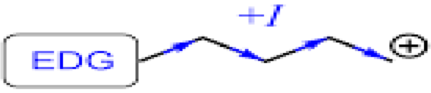


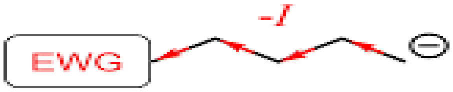
- **Found in:** All carbon atoms that are bonded to four other atoms via single (σ) bonds. This includes all alkanes (e.g., methane CH_4, ethane CH_3CH_3), as well as carbon atoms in alcohols, alkyl halides, and amines where the carbon is saturated. In methane, each of the four sp^3 orbitals overlaps with the 1s orbital of a hydrogen atom to form four identical C-H σ bonds.

sp^2 Hybridization: This occurs when one s orbital and two p orbitals hybridize to form three equivalent sp^2 hybrid orbitals. One p orbital remains unhybridized. The three sp^2 orbitals adopt a trigonal planar arrangement, with bond angles of 120°. The unhybridized p orbital is oriented perpendicular to the plane of the three sp^2 orbitals.



Found in: Carbon atoms involved in a double bond. For example, in ethene ($H_2C{=}CH_2$), each carbon is sp^2 hybridized. Two of the sp^2 orbitals on each carbon form σ bonds with hydrogen atoms, and the third sp^2 orbital forms a σ bond with the other carbon. The unhybridized p orbitals on the two adjacent carbons then overlap sideways, above and below the plane of the σ-bond framework, to form a π bond. Thus, a carbon-carbon double bond consists of one σ bond (from sp^2-sp^2 overlap) and one π bond (from p-p overlap). This model explains the planar structure of alkenes and the restricted rotation around the C=C bond, as rotation would destroy the parallel overlap necessary for the π bond.



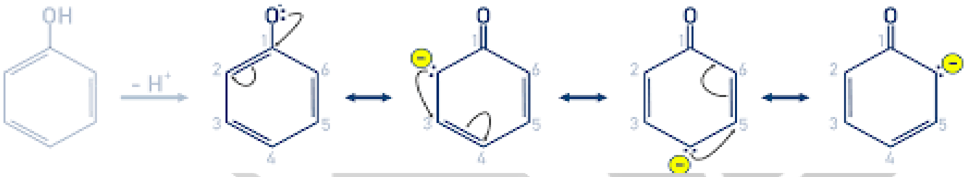


Resonance or Mesomeric Effect (M-Effect):

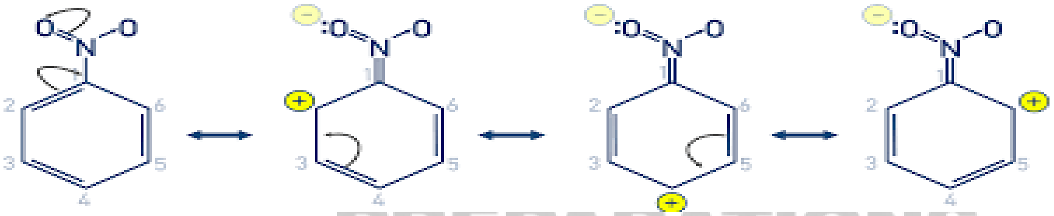
The permanent delocalization of π-electrons or lone pair electrons in a conjugated system (alternating single and double bonds).

The actual molecule is a hybrid of all possible contributing structures (canonical forms).

+M Effect: Electron-donating via resonance (e.g., -OH, $-NH_2$, $-OCH_3$). They donate a lone pair into the π-system.



-M Effect: Electron-withdrawing via resonance (e.g., -CHO, -COOH, $-NO_2$, -CN). They withdraw electrons from the π-system through a double bond.



Electromeric Effect (E-Effect):

A *temporary* effect observed in unsaturated compounds (like alkenes or carbonyls) when attacked by a reagent.

It involves the complete transfer of a shared pair of π-electrons to one of the two atoms, creating a dipole moment for the duration of the attack.

It is reversible and disappears when the attacking reagent is removed.

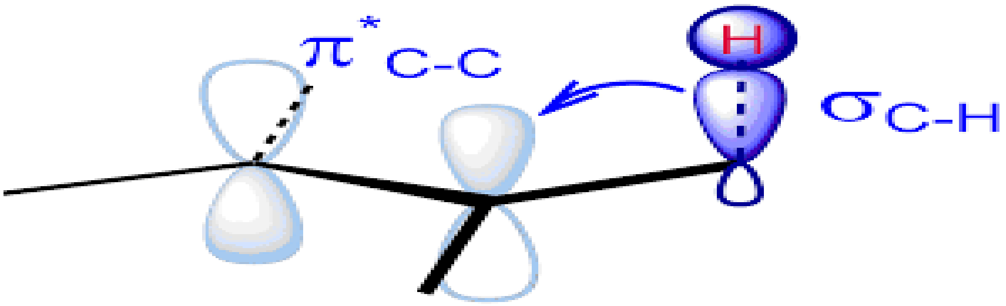
Hyperconjugation:

Also known as **"no-bond resonance,"** it is the stabilizing interaction that results from the delocalization of σ-electrons (usually from a C-H bond) into an adjacent empty or partially filled p-orbital (e.g., in a carbocation) or a π-orbital (e.g., in an alkene).

Applications:

Explains the stability order of carbocations: Tertiary (3°) > Secondary (2°) > Primary (1°).

Explains the stability order of alkenes: More substituted alkenes (with more α-hydrogens) are more stable (Zaitsev's Rule in elimination reactions).



Reaction Intermediates

These are highly reactive, short-lived species formed during the steps of a reaction mechanism.

Intermediate	Formation	Hybridization	Electron Count	Stability Order
Carbocation	Heterolytic cleavage. Positively charged carbon.	sp^2 (Planar)	6 electrons	3° > 2° > 1° > CH_3^+
Carbanion	Heterolytic cleavage. Negatively charged carbon.	sp^3 (Pyramidal)	8 electrons	Stability increases with + and +M groups.
Free Radical	Homolytic cleavage. Neutral with an unpaired electron.	sp^2 (Planar)	7 electrons	3° > 2° > 1° > $CH_3\bullet$
Carbene	Elimination from precursors. Neutral, divalent carbon.	sp^2 (Bent-Singlet) or sp (Linear-Triplet)	6 electrons	Triplet > Singlet

Types of Organic Reactions

Substitution Reaction:

An atom or a group in a molecule is replaced by another atom or group.

Nucleophilic Substitution (SN1, SN2): A nucleophile attacks and replaces a leaving group. Common in alkyl halides.

$CH_3\text{-}Br + OH^- \rightarrow CH_3\text{-}OH + Br^-$

Electrophilic Substitution (SE): An electrophile attacks and replaces a hydrogen atom. Common in aromatic compounds (e.g., Friedel-Crafts alkylation/acylation).

$C_6H_6 + Cl_2$ --($FeCl_3$)--> $C_6H_5\text{-}Cl + HCl$

Free Radical Substitution: A radical replaces another atom. Initiated by heat or light.

$CH_4 + Cl_2$ --(UV Light)--> $CH_3\text{-}Cl + HCl$

Addition Reaction:

Two molecules combine to form a single product, typically involving the breaking of π-bonds.

Electrophilic Addition: An electrophile attacks an alkene or alkyne. Follows Markovnikov's Rule.

$H_2C{=}CH_2 + HBr \rightarrow CH_3\text{-}CH_2\text{-}Br$

Nucleophilic Addition: A nucleophile attacks a polar π-bond, like in carbonyl compounds.

$CH_3\text{-}CHO + HCN \rightarrow CH_3\text{-}CH\ (OH)\text{-}CN$

Topic-wise One-Liners: Organic Chemistry and Reaction Mechanism

Fundamental Concepts of Organic Chemistry

1. Introduction to Organic Chemistry

1. **Organic chemistry** is the study of hydrocarbons and their derivatives.

2. The **Vital Force Theory**, which stated organic compounds could only come from living organisms, was disproved by **Friedrich Wöhler** in 1828.

3. Wöhler synthesized **urea** (an organic compound) from **ammonium cyanate** (an inorganic salt).

2. Unique Properties of Carbon

4. **Catenation** is the unique ability of carbon atoms to form stable covalent bonds with other carbon atoms.

5. Carbon is **tetravalent**, meaning it has four valence electrons and can form four covalent bonds.

6. Carbon can form stable **double ($C=C$)** and **triple ($C\equiv C$) bonds**.

7. **Isomerism** is a major reason for the existence of millions of organic compounds.

3. Classification of Organic Compounds

8. **Acyclic or Open-Chain compounds** contain open chains of carbon atoms which can be straight or branched.

9. **Cyclic or Closed-Chain compounds** contain one or more closed rings of atoms.

10. **Homocyclic or Carbocyclic** compounds have rings consisting of only carbon atoms.

11. **Alicyclic** compounds are ring compounds that resemble aliphatic compounds in properties (e.g., Cyclohexane).

12. **Aromatic** compounds contain at least one benzene ring with delocalized π-electrons (e.g., Benzene, Toluene).

13. **Heterocyclic** compounds have a ring containing at least one atom other than carbon, a **heteroatom** (e.g., O, N, S), like Pyridine and Furan.

4. Functional Groups

14. A **functional group** is an atom or group of atoms that determines the characteristic chemical reactions of a molecule.

15. Key functional groups include Halo (-X), Hydroxyl (-OH), Carbonyl (-C=O), Carboxyl (-COOH), Alkoxy (-O-), Amino ($-NH_2$), Nitro ($-NO_2$), and Cyano ($-C\equiv N$).

5. Structural Features and Bonding

16. **Hybridization** explains the shapes and bonding in organic molecules.

17. In **sp^3 hybridization**, one s and three p orbitals mix to form four equivalent orbitals with **tetrahedral** geometry (~109.5°).

18. **Sp^3 hybridization** is found in alkanes (e.g., CH_4, C_2H_6).

19. In **sp^2 hybridization**, one s and two p orbitals mix to form three equivalent orbitals with **trigonal planar** geometry (~120°).

20. **Sp^2 hybridization** is found in alkenes (e.g., $H_2C=CH_2$); the unhybridized p-orbital forms a **π-bond**.

21. In **sp hybridization**, one s and one p orbital mix to form two equivalent orbitals with **linear** geometry (180°).

22. **sp hybridization** is found in alkynes (e.g., $HC\equiv CH$); the two unhybridized p-orbitals form two **π-bonds**.

Practice MCQs

1. Organic chemistry primarily deals with the study of:

A) Metals and their alloys
B) Hydrocarbons and their derivatives
C) Ionic compounds
D) Noble gases

Answer: Hydrocarbons and their derivatives

2. The Vital Force Theory was disproved by the synthesis of urea from ammonium cyanate by:

A) Berzelius
B) Friedrich Wöhler
C) Lavoisier
D) Arrhenius

Answer: Friedrich Wöhler

3. The ability of carbon to form long chains and rings is called:

A) Tetravalency
B) Isomerism
C) Catenation
D) Hybridization

Answer: Catenation

4. Which of the following is an acyclic compound?

A) Cyclohexane
B) Benzene
C) n-Butane
D) Pyridine

Answer: n-Butane

5. A compound containing a benzene ring is classified as:

A) Alicyclic
B) Aliphatic
C) Aromatic
D) Heterocyclic

Answer: Aromatic

6. Pyridine and Furan are examples of:

A) Carbocyclic compounds
B) Heterocyclic compounds
C) Acyclic compounds
D) Alicyclic compounds

Answer: Heterocyclic compounds

7. The functional group -COOH is known as:

A) Carbonyl
B) Hydroxyl
C) Carboxyl
D) Amino

Answer: Carboxyl

8. The geometry of a carbon atom with sp^3 hybridization is:

A) Linear
B) Trigonal planar
C) Tetrahedral
D) Octahedral

Answer: Tetrahedral

9. In ethene ($H_2C=CH_2$), each carbon atom is:

A) sp hybridized
B) sp^2 hybridized
C) sp^3 hybridized
D) dsp^3 hybridized

Answer: sp^2 hybridized

10. A carbon-carbon triple bond contains:

A) One σ and two π bonds
B) Two σ and one π bond
C) One σ and one π bond
D) Three σ bonds

Answer: One σ and two π bonds

11. Compounds with the same molecular formula but different connectivity are called:

A) Stereoisomers
B) Structural isomers
C) Enantiomers
D) Meso compounds

Answer: Structural isomers

12. n-pentane and isopentane are examples of:

A) Position isomers
B) Functional group isomers
C) Chain isomers
D) Metamers

Answer: Chain isomers

Basic Organic Reaction Mechanisms

Foundations of Organic Reactions

Meaning of an organic reaction

An organic reaction is a chemical transformation in which specific bonds in reactant molecules are broken and new bonds are formed to give products. The material in the uploaded files repeatedly shows that organic chemistry becomes manageable when reactions are organized into patterns rather than memorized as disconnected facts.

Major classes of organic reactions

Organic reactions are commonly grouped as addition, elimination, substitution, and rearrangement reactions. Addition reactions combine two reactants to give one product. Elimination reactions remove atoms or groups and generate a multiple bond. Substitution reactions replace one atom or group with another. Rearrangement reactions reorganize atoms or bonds within a molecule to produce an isomeric product.

Reaction mechanism

A reaction mechanism is the detailed, stepwise description of how reactants are converted into products. A proper mechanism must show which bonds break, which bonds form, the order of events, the intermediates involved, and the relative rates of the elementary steps.

Acid–Base Chemistry as the First Language of Mechanisms

Brønsted–Lowry acids and bases A Brønsted–Lowry acid donates a proton, whereas a Brønsted–Lowry base accepts a proton. When an acid loses H^+, the species formed is its conjugate base. When a base gains H^+, the species formed is its conjugate acid. In water, hydrogen chloride behaves as an acid and water behaves as a base to produce H_3O^+ and Cl^-.

Acids and bases in water In water, hydronium ion is the strongest acid that can exist to any significant extent because any stronger acid transfers its proton completely to water. Hydroxide ion is the strongest base that can exist to any significant extent in water because any stronger base removes a proton from water. This leveling effect is essential for predicting aqueous behavior.

Strong and weak acids Acid strength depends on extent of ionization, not merely on concentration. Strong acids such as HCl, HBr, HI, and the first ionization of H_2SO_4 transfer protons essentially completely in water. Weak acids ionize only partially. Their strengths are expressed by Ka and pKa values. A larger Ka and a smaller pKa correspond to a stronger acid.

Predicting proton-transfer direction Acid–base equilibria favor formation of the weaker acid and the weaker base. In practical terms, proton transfer proceeds from the stronger acid toward the stronger base until the more stable conjugate acid–base pair is reached.

Electron Flow and Curved-Arrow Notation

Curved arrows Curved arrows show the movement of electrons, not the movement of atoms. A full-headed curved arrow indicates movement of an electron pair from a region of higher electron density toward an electron-poor atom or bond.

Rules for correct use The tail of a curved arrow must begin at a lone pair or at a bond, and the head must point toward the atom or bond receiving electrons. The notation must not violate the octet rule for

Topic-wise One-Liners: Basic Organic Reacting Mechanisms

1. **Organic reactions** are understood best through recurring patterns of structural change and recurring mechanistic principles.
2. **Addition reactions** combine two reactants to give a single product, usually by consumption of a π bond.
3. **Elimination reactions** remove atoms or groups from one substrate and generate a multiple bond.
4. **Substitution reactions** replace one group in a substrate with another group.
5. **Rearrangement reactions** convert one structure into an isomer by internal reorganization of bonds.
6. **A reaction mechanism** is the stepwise account of bond breaking, bond making, intermediates, and relative rates.
7. **Homolytic bond cleavage** gives one electron to each fragment and forms radicals.
8. **Heterolytic bond cleavage** gives both bonding electrons to one fragment and forms ions.
9. **Radical reactions** involve species with an odd number of electrons.
10. **Polar reactions** involve species with electron pairs and dominate most organic chemistry.
11. **A Brønsted–Lowry acid** donates a proton.
12. **A Brønsted–Lowry base** accepts a proton.
13. **The conjugate base** is formed when an acid loses $\mathrm{H+}$.
14. **The conjugate acid** is formed when a base gains $\mathrm{H+}$.
15. **HCl in water** produces $\mathrm{H3O+}$ and $\mathrm{Cl-}$.
16. **Hydronium ion** is the strongest acid that persists to any significant extent in water.
17. **Hydroxide ion** is the strongest base that persists to any significant extent in water.
18. **Acid strength** depends on extent of ionization rather than concentration alone.
19. **Strong acids** transfer protons essentially completely in water.
20. **Weak acids** ionize only partially in water.
21. **Ka** is the acidity constant for a weak acid.
22. **A larger Ka** means a stronger acid.
23. **A smaller pKa** means a stronger acid.
24. **Acid–base equilibria** favor the weaker acid and the weaker base.
25. **Curved arrows** show electron flow, not movement of atoms.
26. **A full-headed curved arrow** represents movement of an electron pair.
27. **A fishhook arrow** represents movement of a single electron.
28. **The tail of a curved arrow** begins at a bond or lone pair.
29. **The head of a curved arrow** points toward the electron-accepting atom or bond.
30. **Second-row atoms** should not exceed an octet in ordinary mechanisms.
31. **A Lewis acid** accepts an electron pair.
32. **A Lewis base** donates an electron pair.
33. **$\mathrm{BF3}$** is a Lewis acid because boron is electron-deficient.
34. **$\mathrm{AlCl3}$** is a Lewis acid because aluminum lacks a complete octet.
35. **A carbocation** is an electron-deficient carbon cation and acts as a Lewis acid.

D) Rearrangement

Answer: Rearrangement

5. A detailed stepwise description of how reactants become products is called a:

A) Reaction mechanism
B) Molecular formula
C) Functional group
D) Homologous series

Answer: Reaction mechanism

6. Symmetrical cleavage of a covalent bond is called:

A) Heterolysis
B) Homolysis
C) Ionization
D) Solvation

Answer: Homolysis

7. Unsymmetrical cleavage of a covalent bond in which both electrons go to one fragment is called:

A) Homolysis
B) Heterolysis
C) Hydrolysis
D) Racemization

Answer: Heterolysis

8. A species that contains an unpaired electron is called a:

A) Carbocation
B) Carbanion
C) Radical
D) Nucleophile

Answer: Radical

9. Most common organic mechanisms are:

A) Radical mechanisms
B) Polar mechanisms
C) Nuclear mechanisms
D) Photochemical mechanisms

Answer: Polar mechanisms

10. A Brønsted–Lowry acid is a substance that:

A) Accepts an electron pair
B) Donates a proton
C) Accepts a proton
D) Donates a hydride

Answer: Donates a proton

11. A Brønsted–Lowry base is a substance that:

A) Accepts a proton
B) Donates a proton
C) Accepts a radical
D) Loses an electron pair

Answer: Accepts a proton

12. The species formed when an acid loses a proton is its:

A) Lewis acid
B) Conjugate acid
C) Conjugate base
D) Electrophile

Answer: Conjugate base

13. The species formed when a base gains a proton is its:

A) Conjugate acid
B) Conjugate base
C) Leaving group
D) Electrophile

Answer: Conjugate acid

14. In water, HCl acts as a strong acid because it:

A) Forms a carbocation
B) Transfers its proton essentially completely
C) Becomes a nucleophile
D) Undergoes homolysis

Answer: Transfers its proton essentially completely

15. The strongest acid that can exist to any significant extent in water is:

A) HCl
B) H2SO4
C) H3O+
D) HF

Answer: H3O+

16. The strongest base that can exist to any significant extent in water is:

Aliphatic Hydrocarbons

Functional Groups

Definition: A functional group is a specific group of atoms within a molecule that is responsible for the characteristic chemical reactions of that molecule. The chemistry of every organic molecule, regardless of its size or complexity, is determined by the functional groups it contains.

Key Concept: A given functional group will behave in nearly the same way in every molecule it is a part of. This allows chemists to predict the reactivity of millions of compounds by studying the behavior of a few dozen functional group families.

Major Categories of Functional Groups:

Carbon-Carbon Multiple Bonds:

Alkenes: Contain a carbon-carbon double bond (C=C). Name ending: **-ene**.

Alkynes: Contain a carbon-carbon triple bond (C≡C). Name ending: **-yne**.

Alkanes: Structure and Nomenclature

Definition: Alkanes are a family of saturated hydrocarbons containing only carbon-carbon (C-C) and carbon-hydrogen (C-H) single bonds. They are considered "saturated" because they contain the maximum possible number of hydrogen atoms per carbon.

General Formula: C_nH_{2n+2} (for straight-chain and branched alkanes with no rings).

Key Terms:

Hydrocarbons: Compounds composed only of carbon and hydrogen.

Aliphatic Compounds: Aliphatic compounds are non-aromatic organic compounds (acyclic or alicyclic), including alkanes, alkenes and alkynes.

Isomerism in Alkanes

Definition: Isomers are compounds that have the same molecular formula but different arrangements of atoms.

Constitutional Isomers (or Structural Isomers): Isomers that differ in the connectivity of their atoms—that is, how the atoms are bonded together.

This can involve different carbon skeletons (e.g., butane vs. isobutane).

Different functional groups (e.g., ethanol vs. dimethyl ether, both C_2H_6O).

Different positions of a functional group along a chain.

The number of possible constitutional isomers increases dramatically as the number of carbon atoms increases.

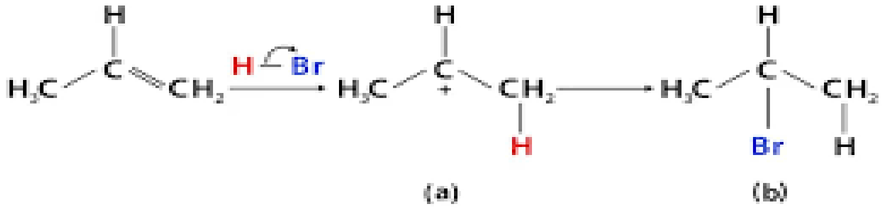
Naming Alkanes (IUPAC Nomenclature)

The IUPAC (International Union of Pure and Applied Chemistry) system provides a systematic method for naming organic compounds. A chemical name has four parts: **Locant-Prefix-Parent-Suffix**.

Rules for Branched-Chain Alkanes:

1. **Find the Parent Hydrocarbon (the Longest Continuous Carbon Chain):**
The parent name is based on the longest continuous chain of carbon atoms. This chain may not

Markovnikov's Rule Basic Mechanism



(a) -hydrogen (H) added to 1° carbon (C) for more stable carbocation

(b) -bromine (Br) added to 2° carbocation to give product

2. Halogenation (Addition of X_2: Cl_2, Br_2)

Mechanism: Electrophilic Addition via a cyclic halonium ion.

Step 1: The alkene's π electrons attack the halogen molecule, forming a cyclic halonium ion (e.g., bromonium ion) and expelling X^-.

Step 2: The nucleophile (X^-) attacks the halonium ion from the side opposite the ring (back-side attack).

Stereochemistry: Anti addition. The two halogen atoms add from opposite faces of the double bond. In cyclic alkanes, this results exclusively in the *Trans* dihalide product.

3. Halohydrin Formation (Addition of HO-X)

Method: Reaction of an alkene with Br_2 or Cl_2 in the presence of water.

Mechanism: Similar to halogenation. The alkene forms a halonium ion. In the presence of water, H_2O acts as the nucleophile (instead of X^-) to open the halonium ion.

Regiochemistry: Markovnikov-like. The -OH group adds to the more highly substituted carbon.

Stereochemistry: Anti addition.

4. Hydration (Addition of Water, H_2O)

Acid-Catalyzed Hydration:

Mechanism: Electrophilic addition of H^+, forming a carbocation, which is then captured by water.

Regiochemistry: Markovnikov.

Used industrially but requires strong acid and high temperatures.

Oxymercuration-Demercuration:

Reagents: 1) $Hg(OAc)_2$, H_2O/THF; 2) $NaBH_4$.

Mechanism: Electrophilic addition of Hg^{2+} forms a mercurinium ion (similar to a halonium ion). Water attacks this ion.

Regiochemistry: Markovnikov. No carbocation rearrangement occurs.

Topic-wise One-Liners: Aliphatic Hydrocarbons & Alkynes

1. Functional Groups

1. A **functional group** is a specific group of atoms within a molecule responsible for its characteristic chemical reactions.
2. The chemistry of an organic molecule is determined by the **functional groups** it contains.
3. **Alkenes** contain a carbon–carbon double bond (C=C) with the name ending **-ene**.
4. **Alkynes** contain a carbon–carbon triple bond (C≡C) with the name ending **-yne**.
5. **Arenes** contain a stable ring with alternating double and single bonds, such as benzene.
6. **Alkyl halides (Haloalkanes)** have a carbon bonded to a halogen (F, Cl, Br, I).
7. **Alcohols** contain a carbon bonded to an **–OH** group, with name ending **-ol**.
8. **Ethers** have two carbon atoms bonded to the same oxygen atom (C–O–C), named with the suffix **ether**.
9. **Amines** contain a carbon bonded to a nitrogen atom, with name ending **-amine**.
10. **Thiols** have a carbon bonded to an **–SH** group, with name ending **-thiol**.
11. **Aldehydes** have at least one hydrogen bonded to the carbonyl carbon (C=O), named with **-al**.
12. **Ketones** have two carbon atoms bonded to the carbonyl carbon, named with **-one**.
13. **Carboxylic acids** contain a carbonyl group bonded to an **–OH** group, named with **-oic acid**.
14. **Esters** contain an ether-like oxygen bonded to the carbonyl carbon, named with **-oate**.
15. **Amides** contain an amine-like nitrogen bonded to the carbonyl carbon, named with **-amide**.

2. Alkanes: Structure & Nomenclature

16. **Alkanes** are saturated hydrocarbons containing only C–C and C–H single bonds.
17. The general formula for alkanes is **C_nH_{2n+2}** (for straight-chain and branched alkanes with no rings).
18. **Hydrocarbons** are compounds composed only of carbon and hydrogen.
19. **Aliphatic compounds** Aliphatic compounds are non-aromatic organic compounds (acyclic or alicyclic), including alkanes, alkenes and alkynes.
20. **Isomers** are compounds with the same molecular formula but different atom arrangements.
21. **Constitutional (structural) isomers** differ in atom connectivity, such as different carbon skeletons or functional group positions.
22. **IUPAC nomenclature** for alkanes follows the format: **Locant–Prefix–Parent–Suffix**.
23. The **parent hydrocarbon** is the longest continuous carbon chain in the molecule.
24. Numbering starts from the end nearer the first branch point.
25. **Alkyl groups** are formed by removing one hydrogen from an alkane, named by replacing **-ane** with **-yl**.
26. Examples: **Methyl ($-CH_3$), Ethyl ($-CH_2CH_3$), Propyl ($-CH_2CH_2CH_3$)**.
27. Branched alkyl groups include **Isopropyl ($(CH_3)_2CH–$)** and **tert-Butyl ($(CH_3)_3C–$)**.
28. **Primary (1°) carbon** is bonded to one other carbon.
29. **Secondary (2°) carbon** is bonded to two other carbons.
30. **Tertiary (3°) carbon** is bonded to three other carbons.

Practice MCQs

1. Which functional group contains a carbon-carbon triple bond?
A) Alkene
B) Alcohol
C) Alkyne
D) Ether
Answer: Alkyne

2. What is the general formula for straight-chain alkanes?
A) C_nH_{2n}
B) C_nH_{2n+2}
C) C_nH_{2n-2}
D) C_nH_n
Answer: C_nH_{2n+2}

3. Which of the following is a constitutional isomer of butane?
A) Propane
B) Isobutane
C) Cyclobutane
D) Pentane
Answer: Isobutane

4. In IUPAC naming, the "parent" refers to what?
A) The longest carbon chain
B) The substituents
C) The functional group
D) The locants
Answer: The longest carbon chain

5. What is the name of the group $–CH_2CH_3$?
A) Methyl
B) Ethyl
C) Propyl
D) Butyl
Answer: Ethyl

6. A carbon atom bonded to three other carbons is classified as:
A) Primary
B) Secondary
C) Tertiary
D) Quaternary
Answer: Tertiary

7. Which conformation of ethane has the lowest energy?
A) Eclipsed
B) Staggered
C) Gauche
D) Anti
Answer: Staggered

8. What type of strain is responsible for the higher energy of eclipsed conformations?
A) Steric strain
B) Torsional strain
C) Angle strain
D) Ring strain
Answer: Torsional strain

9. Which reaction of alkenes gives anti addition of halogens?
A) Hydrogenation
B) Halogenation
C) Hydration
D) Hydroboration
Answer: Halogenation

10. According to Markovnikov's rule, in the addition of HBr to propene, bromine adds to:
A) The carbon with more hydrogens
B) The carbon with fewer hydrogens
C) Either carbon equally
D) The double bond carbon with no hydrogen
Answer: The carbon with fewer hydrogens

11. What reagent is used for syn hydroxylation of alkenes to give cis-1,2-diols?
A) O_3
B) OsO_4
C) H_2SO_4
D) BH_3
Answer: OsO_4

12. Which method gives anti-Markovnikov addition of water to an alkene?
A) Oxymercuration-demercuration
B) Acid-catalyzed hydration
C) Hydroboration-oxidation

Aromatic Compounds (Benzene)

Introduction to Aromatic Compounds

Definition: Aromatic compounds are a class of cyclic, planar, and conjugated organic compounds that exhibit exceptional stability due to the delocalization of π-electrons. The term "aromatic" originally referred to their pleasant fragrances but now is based on their specific chemical structure and stability.

Parent Molecule: Benzene (C_6H_6) is the fundamental and simplest aromatic hydrocarbon. All compounds that resemble benzene in chemical behavior, particularly their unusual stability, are classified as aromatic.

Historical Context:

Michael Faraday first isolated benzene in 1825 from the oily residue of London's illuminating gas.

Eilhardt Mitscherlich synthesized it in 1834 by heating benzoic acid with lime.

The name "**benzene**" is derived from "gum benzoin," a fragrant resin from which benzoic acid was obtained.

Health Warning: Benzene is a known carcinogen (causes leukemia) and should be handled with extreme care.

Nomenclature of Benzene Derivatives

The systematic process of naming benzene derivatives follows IUPAC rules, though many common names are retained.

Monosubstituted Benzenes: Compounds with one substituent on the benzene ring.

IUPAC System: Named by adding the substituent name as a prefix to "benzene."

Example: $C_6H_5\text{–}Br$ is **Bromobenzene**; $C_6H_5\text{–}NO_2$ is **Nitrobenzene**.

Common Names: Some derivatives have widely accepted common names that are used in preference to systematic names.

$C_6H_5\text{–}CH_3$: **Toluene** (not Methylbenzene)

$C_6H_5\text{–}OH$: **Phenol** (not Hydroxybenzene)

$C_6H_5\text{–}NH_2$: **Aniline** (not Aminobenzene)

$C_6H_5\text{–}CHO$: **Benzaldehyde**

$C_6H_5\text{–}COOH$: **Benzoic Acid**

Disubstituted Benzenes

Compounds with two substituents. The relative positions are indicated by prefixes or numbers.

Ortho (o- or 1, 2): Substituents are on adjacent carbon atoms.

Meta (m- or 1, 3): Substituents are separated by one carbon atom.

Para (p- or 1, 4): Substituents are on opposite sides of the ring.

The Phenyl (C_6H_5–) and Benzyl (C_6H_5—CH_2–) Groups:

Phenyl Group (Ph- or φ-): The group derived from benzene by removing one hydrogen atom. It is used when the benzene ring is a substituent on a larger molecule.

Topic Wise One Liner: Aromatic Compounds

1. Aromatic compounds are cyclic, planar, conjugated, and obey Hückel's (4n+2) π-electron rule.
2. Benzene (C_6H_6) is the parent aromatic hydrocarbon with a delocalized π-cloud of 6 electrons.
3. The resonance energy of benzene is **152 kJ/mol**, explaining its exceptional stability.
4. Benzene primarily undergoes **Electrophilic Aromatic Substitution (EAS)** reactions to preserve its aromaticity.
5. The EAS mechanism involves the formation of a resonance-stabilized **arenium ion** intermediate.
6. Substituents on the ring are classified as **Activating/Deactivating** and **Ortho-Para/Meta Directing**.
7. **Ortho/Para directors** are generally electron-donating groups (except halogens).
8. **Meta directors** are strong electron-withdrawing groups.
9. The benzene ring is resistant to addition and oxidation, but alkyl side-chains can be oxidized to –COOH.

Aromatic Compounds & Electrophilic Aromatic Substitution: Detailed One-Liners

1. Introduction & History

10. **Aromatic compounds** are a class of cyclic, planar, and conjugated organic compounds that exhibit exceptional stability due to the delocalization of π-electrons.

11. **Benzene (C_6H_6)** is the simplest and parent aromatic hydrocarbon.

12. **Michael Faraday** first isolated benzene in 1825 from the oily residue of coal gas.

13. **Eilhardt Mitscherlich** synthesized benzene by heating benzoic acid with lime in 1834.

14. The name "benzene" is derived from "gum benzoin," a fragrant resin from which benzoic acid was obtained.

15. Benzene is a known **carcinogen** and can cause **leukemia and leukopenia.** (Benzene exposure is linked to **leukemia** and also **bone-marrow suppression** which can cause **leukopenia/aplastic anemia.)**

2. Nomenclature of Benzene Derivatives

7. **Monosubstituted benzenes** are named by adding the substituent as a prefix to "benzene" (e.g., C_6H_5–Br is Bromobenzene).

8. Common names for monosubstituted benzenes include **Toluene** (C_6H_5–CH_3), **Phenol** (C_6H_5–OH), **Aniline** (C_6H_5–NH_2), **Benzaldehyde** (C_6H_5–CHO), and **Benzoic acid** (C_6H_5–COOH).

9. For **disubstituted benzenes**, **ortho (o-)** denotes a 1, 2 relationship, **Meta (m-)** denotes a 1, 3 relationship, and **para (p-)** denotes a 1, 4 relationship.

10. If one substituent gives a special name (like -OH in phenol), the compound is named as a derivative of that parent, with the special group at position 1 (e.g., NO_2–C_6H_4–OH is **o**-Nitrophenol).

11. In **polysubstituted benzenes**, the ring is numbered to give the lowest possible set of locants to the substituents, which are listed in alphabetical order.

12. The **Phenyl group (Ph- or C_6H_5–)** is the group derived from benzene by removing one hydrogen

11. Spectroscopy of Aromatic Compounds

58. In IR spectroscopy, aromatic C–H stretching occurs near **3030 cm^{-1}**, and the ring itself shows absorptions between **1450 to 1600 cm^{-1}**.

59. In **^1H NMR**, aromatic protons are strongly deshielded by the **ring current** and absorb between **6.5 and 8.0 δ**.

60. Benzylic protons ($H–C–C_6H_5$) absorb between **2.3 and 3.0 δ**.

Practice MCQs

1. Which scientist first isolated benzene in 1825 from coal gas?
A) August Kekulé
B) Eilhardt Mitscherlich
C) Michael Faraday
D) Richard Willstätter
Answer: Michael Faraday

2. The synthesis of benzene by heating benzoic acid with lime was achieved by:
A) Faraday
B) Kekulé
C) Mitscherlich
D) Hückel
Answer: Mitscherlich

3. Benzene is known to be:
A) A strong base
B) A carcinogen
C) An aliphatic hydrocarbon
D) Highly saturated
Answer: A carcinogen

4. What is the common name for $C_6H_5–CH_3$?
A) Phenol
B) Aniline
C) Toluene
D) Benzaldehyde
Answer: Toluene

5. The compound $C_6H_5–OH$ is commonly known as:
A) Toluene
B) Phenol
C) Aniline
D) Benzoic acid
Answer: Phenol

6. What is the IUPAC name for $C_6H_5–NH_2$?
A) Hydroxybenzene
B) Benzenamine
C) Methylbenzene
D) Nitrobenzene
Answer: Benzenamine

7. For disubstituted benzenes, the prefix "meta" indicates which positions?
A) 1,2
B) 1,3
C) 1,4
D) 1,5
Answer: 1,3

8. The group $C_6H_5CH_2–$ is known as:
A) Phenyl
B) Benzyl
C) Phenoxide
D) Toluene
Answer: Benzyl

9. The phenyl group is represented as:
A) Bn–
B) Ph–
C) Tol–
D) Benz–
Answer: Ph–

10. Kekulé's structure of benzene failed to explain:
A) Planarity
B) Identical bond lengths
C) sp^2 hybridization
D) Resonance energy
Answer: Identical bond lengths

Halogenoalkanes (Alkyl Halides)
And SN Reactions

Introduction to Halogenoalkanes

Definition: Halogenoalkanes, also known as alkyl halides, are organic compounds in which one or more hydrogen atoms of an alkane have been replaced by halogen atoms (F, Cl, Br, I). Their general formula is **R-X**.

Or

Monohalo alkanes (R-X) are called alkyl halides.

It is a class of compounds where Halogen is bonded to the **carbon atom (typically sp³-hybridized)** of an alkyl group via an σ(C–X) bond."

Halogenoarenes: These are compounds where a halogen is attached directly to an aromatic ring. Their general formula is **Ar-X** (where Ar is an aryl group, e.g., C_6H_5-).

Classification of Alkyl Halides

Alkyl halides are classified based on the carbon atom to which the halogen is bonded.

Primary (1°) Alkyl Halide: The halogen atom is attached to a carbon atom that is itself attached to only one other carbon atom.

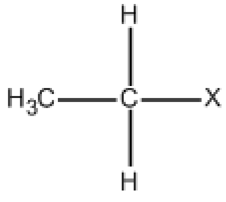
Examples: CH_3-Cl (Chloromethane), CH_3-CH_2-Br (Bromoethane).

Secondary (2°) Alkyl Halide: The halogen atom is attached to a carbon atom that is attached to two other carbon atoms.

Example: $(CH_3)_2CH$-Cl (2-Chloropropane or Isopropyl chloride).

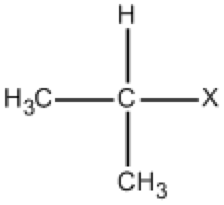
Tertiary (3°) Alkyl Halide: The halogen atom is attached to a carbon atom that is attached to three other carbon atoms.

Example: $(CH_3)_3C$-Cl (2-Chloro-2-methylpropane or tert-Butyl chloride)



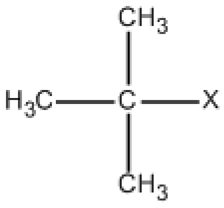
$H_3C-\overset{H}{\underset{H}{C}}-X$

Primary



$H_3C-\overset{H}{\underset{CH_3}{C}}-X$

Secondary



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-X$

Tertiary

Remember

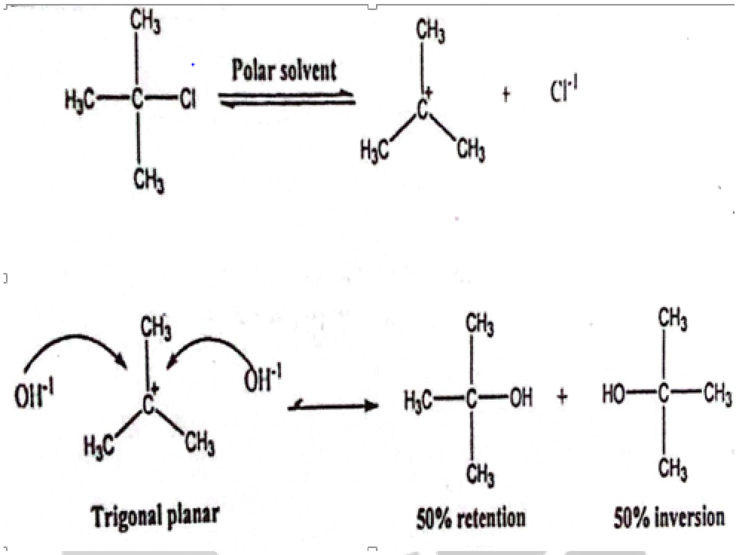
$\alpha -$ Carbon: Carbon to which functional group is directly attached.

$\alpha -$Hydrogen: hydrogen atoms attached to $\alpha -$carbon atoms.

Preparation of Halogenoalkanes and Halogenoarenes

From Alkanes (Free Radical Halogenation): Alkanes react with halogens (Cl_2 or Br_2) in the presence of UV light to form alkyl halides. This reaction proceeds via a free radical mechanism and often gives a mixture of mono- and poly-halogenated products.

The SN^1 Mechanism (Substitution Nucleophilic Unimolecular)



Mechanism: A **two-step** process.

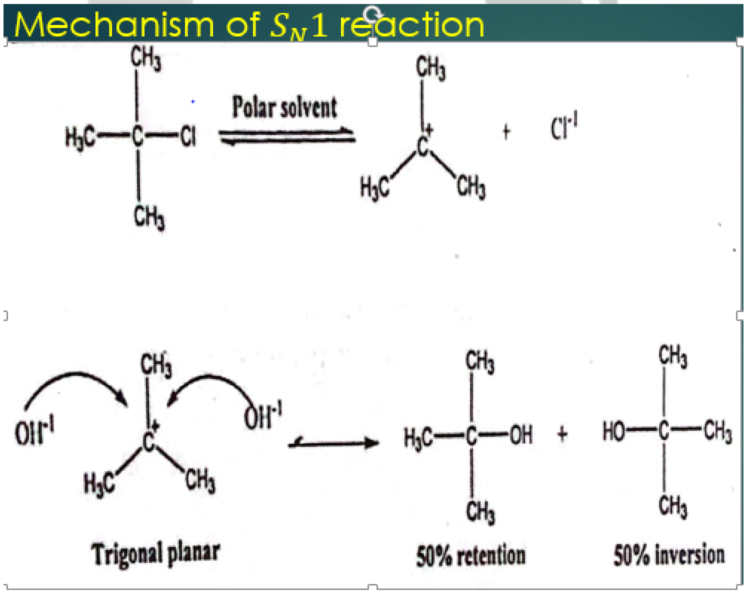
Slow, Rate-Limiting Step: Spontaneous dissociation of the alkyl halide to form a planar **carbocation intermediate**.

Fast Step: The nucleophile attacks the carbocation from either side to form the product.

Kinetics: First-order. Rate = k [R-X]

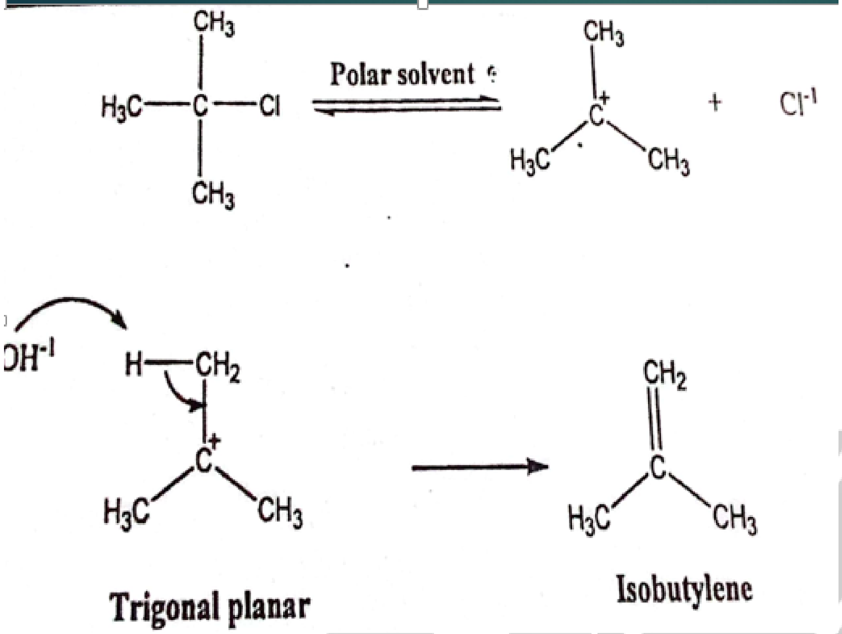
Stereochemistry: Results in **racemization** (a mixture of both enantiomers) because the planar carbocation is attacked equally from both faces. However, in practice, often a slight excess of inversion is observed due to "ion-pair" effects where the leaving group partially blocks one side.

Factors Affecting SN^1 Reactivity:



Substrate (Stability of the Carbocation): The rate depends on the stability of the carbocation formed. **Tertiary** > **Secondary** >

Mechanism of E1 reaction



The E1cB Mechanism (Elimination, Unimolecular from the Conjugate Base)

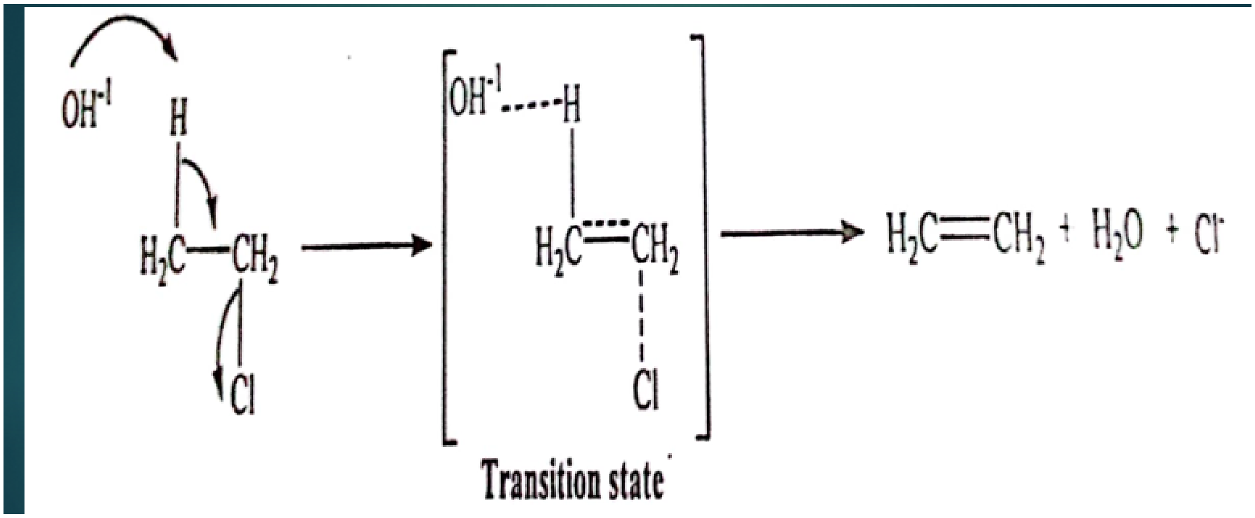
Mechanism: A **two-step** process common in poor leaving groups with an acidic β-hydrogen (e.g., adjacent to a carbonyl group).

Fast Step: A base abstracts a β-proton to form a **carbanion intermediate**.

Slow, Rate-Limiting Step: In E1cB, mechanism varies: if **carbanion formation** is rate-limiting → E1cB$_{rev}$,if **leaving group departure** is rate-limiting → E1cB$_{irrev}$

Kinetics: Complex, but often first-order in base.

This mechanism is predominant in biological systems.



Topic-wise One-Liners: Halogenoalkanes (Alkyl Halides) And SN Reactions

1. Introduction & Nomenclature of Alkyl Halides

1. **Halogenoalkanes** or **alkyl halides** are organic compounds with the general formula **R-X**, where a halogen atom (F, Cl, Br, I) replaces a hydrogen in an alkane.
2. **Halogenoarenes** have the general formula **Ar-X**, where the halogen is attached directly to an aromatic ring.
3. Alkyl halides are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)** based on the carbon atom to which the halogen is bonded.
4. In a **primary alkyl halide**, the halogen-bearing carbon is attached to only one other carbon atom.
5. In a **secondary alkyl halide**, the halogen-bearing carbon is attached to two other carbon atoms.
6. In a **tertiary alkyl halide**, the halogen-bearing carbon is attached to three other carbon atoms.
7. In IUPAC nomenclature, the parent chain is numbered to give the halogen the lowest possible locant.

2. Physical Properties & Structure of Alkyl Halides

8. Lower members like CH_3Cl and C_2H_5Cl are gases, while higher members are liquids or solids.
9. Alkyl halides are generally **insoluble in water** due to their inability to form hydrogen bonds.
10. Boiling points follow the order: **RI > RBr > RCl > RF** for the same alkyl group due to increasing molecular mass and van der Waals forces.
11. The **C-X bond is polar** because halogens are more electronegative than carbon, creating a δ^+ charge on carbon and a δ^- charge on halogen.
12. The **C-X bond strength** decreases down the group: **C-F > C-Cl > C-Br > C-I**.
13. The carbon atom in alkyl halides is **sp^3 hybridized** with a tetrahedral geometry.

3. Preparation of Alkyl Halides

14. Alkanes undergo **free radical halogenation** with Cl_2 or Br_2 in UV light to yield a mixture of alkyl halides.
15. Alkenes react with **hydrogen halides (HX)** via electrophilic addition, following **Markovnikov's rule**.
16. A common laboratory method involves the reaction of **alcohols with HX**; tertiary alcohols react the fastest.
17. **Thionyl chloride ($SOCl_2$)** converts alcohols to alkyl chlorides, producing gaseous SO_2 and HCl.
18. **Phosphorus trihalides (PBr_3, PCl_3)** are used to prepare alkyl bromides and chlorides from alcohols.
19. Halogenoarenes like chlorobenzene are prepared by the **electrophilic aromatic substitution** of benzene using Cl_2 and a Lewis acid catalyst (e.g., $FeCl_3$).

4. Nucleophilic Substitution Reactions (SN Reactions)

20. A **nucleophilic substitution reaction** involves a nucleophile (Nu^-) replacing a leaving group (X^-) in an alkyl halide.
21. The **substrate** is the alkyl halide (R-X) undergoing the reaction.
22. A **nucleophile** is an electron-rich species (e.g., HO^-, CN^-, NH_3) that attacks the electrophilic carbon.
23. A **leaving group** is the atom or group displaced from the substrate; the best leaving groups are

Practice MCQs

1. What is the general formula for alkyl halides?
A) R-OH
B) R-X
C) R-COOH
D) R-NH_2
Answer: R-X

2. In halogenoarenes, the halogen is attached to which type of carbon?
A) sp^3 hybridized carbon of an alkyl group
B) sp^2 hybridized carbon of an aromatic ring
C) sp hybridized carbon of an alkyne
D) Carbon of a carbonyl group
Answer: sp^2 hybridized carbon of an aromatic ring

3. A primary alkyl halide has the halogen attached to a carbon bonded to how many other carbon atoms?
A) One
B) Two
C) Three
D) Zero
Answer: One

4. Which of the following is a secondary alkyl halide?
A) CH_3CH_2Br
B) $(CH_3)_2CHCl$
C) $(CH_3)_3CBr$
D) CH_3Cl
Answer: $(CH_3)_2CHCl$

5. The α-carbon in an alkyl halide is defined as:
A) The carbon adjacent to the halogen
B) The carbon to which the functional group is directly attached
C) The carbon farthest from the halogen
D) The carbon bearing the most hydrogens
Answer: The carbon to which the functional group is directly attached

6. Which method is NOT typically used for preparing alkyl halides from alcohols?
A) Reaction with HX
B) Reaction with $SOCl_2$
C) Reaction with $KMnO_4$
D) Reaction with PBr_3
Answer: Reaction with $KMnO_4$

7. Halogenation of benzene to form chlorobenzene is an example of:
A) Nucleophilic aromatic substitution
B) Electrophilic aromatic substitution
C) Free radical substitution
D) Nucleophilic addition
Answer: Electrophilic aromatic substitution

8. For a given alkyl group, the boiling point order of alkyl halides is:
A) RF > RCl > RBr > RI
B) RI > RBr > RCl > RF
C) RCl > RBr > RI > RF
D) RBr > RI > RCl > RF
Answer: RI > RBr > RCl > RF

9. The carbon-halogen bond strength decreases in the order:
A) C-F > C-Cl > C-Br > C-I
B) C-I > C-Br > C-Cl > C-F
C) C-Cl > C-Br > C-F > C-I
D) C-Br > C-Cl > C-I > C-F
Answer: C-F > C-Cl > C-Br > C-I

10. A nucleophile is best described as:
A) An electron-deficient species
B) An electron-rich species that donates an electron pair
C) A species that accepts a proton
D) A strong acid
Answer: An electron-rich species that donates an electron pair

11. Which of the following is a strong nucleophile and a good leaving group?
A) OH^-
B) I^-
C) NH_2^-
D) F^-
Answer: I^-

12. The overall reactivity order of alkyl halides (for a particular alkyl group) towards

Alcohols and Phenols

Introduction to Alcohols and Phenols

Alcohols and phenols are classes of organic compounds characterized by the presence of a hydroxyl (-OH) functional group.

Alcohols: The hydroxyl group is attached to a saturated carbon (typically sp^3-hybridized) in an aliphatic system". Their general formula is **R–OH**.

Phenols: The hydroxyl group is directly bonded to a sp^2-hybridized carbon atom of an aromatic ring. The simplest phenol is **C_6H_5OH**.

They can be viewed as organic derivatives of water (H–O–H), where one hydrogen atom is replaced by an alkyl group (alcohol) or an aryl group (phenol).

ALCOHOLS

Classification of Alcohols

Alcohols are classified based on the number of hydroxyl groups and the degree of substitution of the carbon atom bearing the -OH group.

Based on the Number of -OH Groups:

Monohydric: Contain one -OH group (e.g., Ethanol, CH_3CH_2OH).

Dihydric: Contain two -OH groups. They are called **glycols** (e.g., Ethylene glycol, $HO\text{-}CH_2\text{-}CH_2\text{-}OH$).

Trihydric: Contain three -OH groups (e.g., Glycerol or Glycerine, $HO\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}OH$).

Polyhydric: Contain many -OH groups.

Based on the Carbon Atom Bearing the -OH Group:

Primary (1°): The -OH group is attached to a carbon that is bonded to only one other carbon atom. (e.g., CH_3CH_2OH).

Secondary (2°): The -OH group is attached to a carbon that is bonded to two other carbon atoms. (e.g., $(CH_3)_2CHOH$).

Tertiary (3°): The -OH group is attached to a carbon that is bonded to three other carbon atoms. (e.g., $(CH_3)_3COH$).

Nomenclature of Alcohols

IUPAC System:

1. Select the longest continuous carbon chain that contains the hydroxyl group.
2. Replace the "-e" of the parent alkane with the suffix "**-ol**".
3. Number the chain to give the carbon bearing the -OH group the lowest possible number. This locant is placed before the parent name or the suffix "-ol".
4. Name and number any substituents (alkyl groups, halogens) in alphabetical order.
5. In cyclic alcohols, the -OH group is assumed to be on C-1.
6. For polyhydric alcohols, use suffixes like "**-diol**", "**-triol**", etc., with appropriate locants.

Examples:

CH_3OH: Methanol

$CH_3CH_2CH_2OH$: Propan-1-ol

$(CH_3)_2CHOH$: Propan-2-ol

$CH_3CH_2CH(OH)CH_3$: Butan-2-ol

$(CH_3)_3COH$: 2-Methylpropan-2-ol

$HO\text{-}CH_2\text{-}CH_2\text{-}OH$: Ethane-1, 2-diol

Topic Wise One Liners on Alcohols and Phenols

Introduction and Definition

1. **Alcohols** are organic compounds where a hydroxyl (**-OH**) group is attached to a saturated, **sp^3-hybridized carbon** atom in an aliphatic chain.
2. **Phenols** are organic compounds where the **-OH group** is directly bonded to an **sp^2-hybridized carbon** of an aromatic ring.
3. Both alcohols and phenols can be considered as organic derivatives of **water (H-O-H)** where one hydrogen is replaced by an alkyl or aryl group.

Classification of Alcohols

4. **Monohydric alcohols** contain only one **-OH** group (e.g., Ethanol).
5. **Polyhydric alcohols** contain more than one **-OH** group.
6. **Dihydric alcohols** (Glycols) have two -OH groups (e.g., Ethylene glycol).
7. **Trihydric alcohols** have three -OH groups (e.g., Glycerol or Glycerine).
8. A **primary (1°) alcohol** has its **-OH group attached to a carbon** atom that is bonded to only **one other carbon** atom.
9. A **secondary (2°) alcohol** has its **-OH group attached to a carbon** atom that is bonded to **two other carbon** atoms.
10. A **tertiary (3°) alcohol** has its **-OH group attached to a carbon** atom that is bonded to **three other carbon** atoms.

Nomenclature of Alcohols and Phenols

11. In the **IUPAC system**, the suffix **"-ol"** is used for alcohols, replacing the "-e" of the parent alkane.
12. The carbon chain is numbered to give the **carbon bearing the -OH group the lowest possible number**.
13. For **polyhydric alcohols**, suffixes like **"-diol"** and **"-triol"** are used.
14. **Phenols** are named as derivatives of the parent compound "phenol," with the -OH group at carbon 1.
15. Common names like *tert*-butyl alcohol, benzyl alcohol, and ethylene glycol are accepted by IUPAC.

Structure and Physical Properties

16. The oxygen atom in alcohols is **sp^3-hybridized**, with a **C-O-H bond angle of approximately 105°–108.5°**.
17. Alcohols and phenols have **higher boiling points** than comparable alkanes or alkyl halides due to **intermolecular hydrogen bonding**.
18. Boiling point decreases with **increased branching** in isomeric alcohols due to a decrease in surface area.
19. Lower alcohols (C1-C3) are **miscible with water** due to hydrogen bonding; solubility decreases with increasing alkyl chain length.
20. Phenol is a colorless, crystalline solid with a characteristic odor and is **sparingly soluble** in cold water.

Acidity of Alcohols and Phenols

21. Alcohols are **very weak acids**, with pKa values ranging from **15.5 to 18**.
22. The order of acidity for alcohols is: **Methanol > Primary > Secondary > Tertiary**.
23. Alcohols react with **active metals** like sodium (Na) to liberate hydrogen gas and form **alkoxides**.
24. Alcohols **do not react with weak bases** like NaOH or NaHCO$_3$ in aqueous solution.

78. In ^{1}H **NMR**, the -OH proton appears as a broad singlet, typically between **1-5 δ**, which often disappears on shaking with D_2O.
79. Protons on the carbon bearing the -OH group (H-C-O) are deshielded and appear between **3.4-4.5 δ**.
80. In ^{13}C **NMR**, the carbon attached to the -OH group is deshielded and absorbs in the range **50-80 δ**.
81. In **Mass Spectrometry**, alcohols often show a weak molecular ion peak and common fragments due to **alpha cleavage** (m/z 31 for $CH_2=OH^+$) and **dehydration (M-18)**.

Practice MCQs

1) Which of the following is a tertiary alcohol?

A) Ethanol
B) 2-Propanol
C) 2-Methyl-2-propanol
D) 1-Butanol

Answer: 2-Methyl-2-propanol

2) The oxygen atom in alcohols is:

A) sp hybridized
B) sp^2 hybridized
C) sp^3 hybridized
D) Not hybridized

Answer: sp^3 hybridized

3) Which alcohol is most acidic?

A) Methanol
B) Ethanol
C) 2-Propanol
D) 2-Methyl-2-propanol

Answer: Methanol

4) Phenols are more acidic than alcohols because:

A) The phenoxide ion is resonance stabilized
B) Phenols have higher molecular weight
C) Phenols are soluble in water
D) Phenols contain an aromatic ring

Answer: The phenoxide ion is resonance stabilized

5) Which reagent is used to distinguish between 1°, 2°, and 3° alcohols(C1-C6)?

A) Tollen's reagent
B) Fehling's solution
C) Lucas reagent
D) Benedict's solution

Answer: Lucas reagent

6) Primary alcohols on oxidation with mild oxidizing agent yield:

A) Ketones
B) Aldehydes
C) Carboxylic acids
D) Esters

Answer: Aldehydes

7) Which of the following is not a method for preparing alcohols?

A) Hydration of alkenes
B) Reduction of aldehydes
C) Single step oxidation of alkanes
D) Grignard reaction

Answer: Single step oxidation of alkanes

8) The IUPAC name of $CH_3CH_2CH_2OH$ is:

A) Ethanol
B) Propan-1-ol
C) Butan-1-ol
D) Methanol

Answer: Propan-1-ol

9) Which alcohol cannot be oxidized by $K_2Cr_2O_7/H_2SO_4$?

A) Methanol
B) Ethanol
C) 2-Propanol
D) 2-Methyl-2-propanol

Answer: 2-Methyl-2-propanol

10) Phenol reacts with bromine water to give:

A) m-Bromophenol
B) 2,4,6-Tribromophenol
C) p-Bromophenol
D) Bromobenzene

Answer: 2,4,6-Tribromophenol

11) Which of the following is a dihydric alcohol?

Carbonyl Compounds – Aldehydes, Ketones, and Carboxylic Acid Derivatives (Nu.Addition Reactions)

Introduction to Carbonyl Compounds

Definition: Carbonyl compounds are a major class of organic molecules characterized by the presence of a **carbonyl functional group**, which consists of a carbon atom doubly bonded to an oxygen atom (>C=O).

Significance: This group is highly reactive and is a key structural feature in many biological molecules (like sugars and metabolic intermediates) and industrial chemicals (like solvents, pharmaceuticals, and polymers).

Major Classes:

The nature of the atoms or groups attached to the carbonyl carbon determines the class of the compound and its reactivity.

Aldehydes (R-CHO): The carbonyl carbon is bonded to at least one hydrogen atom.

Ketones (R-CO-R'): The carbonyl carbon is bonded to two alkyl or aryl groups.

Carboxylic Acids (R-COOH): Carboxylic acids contain the carboxyl group (-COOH), where the carbonyl carbon is bonded to a hydroxyl group. The carboxyl group is a resonance hybrid, making it significantly more acidic than alcohols

Carboxylic Acid Derivatives:

Esters (R-COO-R')

Amides (R-CONH$_2$, R-CONHR, R-CONR$_2$)

Acyl Chlorides (R-COCl)

Acid Anhydrides (R-CO-O-CO-R')

Remember

Reducing sugars possess a free aldehyde group or a free hemiacetal/hemiketal group capable of reducing mild oxidizing agents (**Tollen's, Fehling's, Benedict's).** All monosaccharides (both aldoses and ketoses) are reducing because ketoses tautomerize to aldoses under basic conditions. **Disaccharides** are reducing if they have a free anomeric carbon (maltose, lactose) and non-reducing if both anomeric carbons are bonded (sucrose). It is the principal constituent of number of essential oils used as fragrances and flavours.

Aldehydes and Ketones

Nomenclature of Aldehydes

Aldehydes

IUPAC System

Rule: Select the longest continuous carbon chain containing the -CHO group.

Suffix: Replace the final "-e" of the parent alkane with "**-al**".

Numbering: The carbonyl carbon is always assigned number **1**. It is not necessary to specify its position in the name.

Examples:

HCHO: Methanal

CH_3CHO: Ethanal

For Cyclic Aldehydes

Topic Wise Liner on Carbonyl Compounds

1. Introduction to Carbonyl Compounds

1. Organic compounds containing the **carbonyl functional group** (>C=O) are called carbonyl compounds.
2. The carbonyl group consists of a carbon atom doubly bonded to an oxygen atom.
3. Major classes include **aldehydes**, **ketones**, **carboxylic acids**, and their **derivatives** (esters, amides, acyl chlorides, acid anhydrides).
4. In **aldehydes**, the carbonyl carbon is bonded to at least one hydrogen atom (R-CHO).
5. In **ketones**, the carbonyl carbon is bonded to two alkyl or aryl groups (R-CO-R').
6. Aldehydes are terminal functional groups and have no position isomerism.

2. Nomenclature

7. The IUPAC suffix for aldehydes is **-al**.

8. In IUPAC naming of aldehydes, the carbonyl carbon is always assigned number **1**.

9. For cyclic aldehydes where -CHO is attached to a ring, the suffix **-carbaldehyde** is used.

10. The IUPAC suffix for ketones is **-one**.

11. In ketones, the chain is numbered to give the carbonyl carbon the **lowest possible number**.

12. Common names for ketones are derived by naming the two alkyl groups followed by the word **"ketone"**.

3. Structure and Physical Properties

13. The carbonyl carbon is **sp^2-hybridized**, resulting in a **trigonal planar** geometry with bond angles of ~120°.

14. The C=O bond is **polar** due to the electronegativity difference between carbon and oxygen.

15. Carbonyl compounds have **higher boiling points** than alkanes of similar molecular weight due to **dipole-dipole interactions**.

16. They have **lower boiling points** than comparable alcohols because they **cannot form intermolecular hydrogen bonds** with each other.

17. Lower members (up to C_4) are **soluble in water** as the carbonyl oxygen can hydrogen bond with water.

4. Preparation of Aldehydes and Ketones

18. **Primary alcohols** undergo controlled oxidation to form **aldehydes** using reagents like **PCC** or **Dess-Martin Periodinane**.

19. **Secondary alcohols** are oxidized to **ketones** by common oxidizing agents like $K_2Cr_2O_7/H_2SO_4$.

20. **Ozonolysis of alkenes** followed by reduction with Zn/H_2O yields aldehydes and/or ketones.

21. **Hydration of terminal alkynes** (e.g., HC≡CH) produces **aldehydes**.

22. **Hydration of internal alkynes** produces **ketones**.

23. **Friedel-Crafts Acylation** of an aromatic ring with an acid chloride produces **aryl ketones**.

24. Formaldehyde is prepared industrially by the oxidation of **methanol vapors** over a catalyst like FeO/Mo_2O_3.

25. Acetaldehyde is prepared in the lab by the oxidation of **ethanol** with acidified $Na_2Cr_2O_7$.

26. Acetone is prepared by the **dry distillation of calcium acetate**.

27. Partial reduction of **esters** using **DIBAL-H** at low temperatures yields aldehydes.

Practice MCQs

1. The carbonyl functional group is characterized by which of the following?
A) C-O single bond
B) C≡O triple bond
C) C=O double bond
D) C-OH bond
Answer: C=O double bond

2. Which class of carbonyl compounds has the carbonyl carbon bonded to at least one hydrogen atom?
A) Ketones
B) Carboxylic acids
C) Aldehydes
D) Esters
Answer: Aldehydes

3. The IUPAC suffix for naming aldehydes is:
A) -one
B) -al
C) -oic acid
D) -ol
Answer: -al

4. In the IUPAC naming of aldehydes, the carbonyl carbon is assigned which number?
A) The lowest possible number
B) Number 1
C) Number 2
D) The highest possible number
Answer: Number 1

5. For cyclic aldehydes where the -CHO group is attached directly to a ring, the suffix used is:
A) -al
B) -aldehyde
C) -carbaldehyde
D) -cycloaldehyde
Answer: -carbaldehyde

6. The IUPAC suffix for ketones is:
A) -al
B) -one
C) -ene
D) -ol
Answer: -one

7. In ketones, the parent chain is numbered to give the carbonyl carbon:
A) The highest possible number
B) Number 1
C) The lowest possible number
D) Any arbitrary number
Answer: The lowest possible number

8. The hybridization state of the carbonyl carbon in aldehydes and ketones is:
A) sp
B) sp^2
C) sp^3
D) dsp^2
Answer: sp^2

9. The geometry around the carbonyl carbon is:
A) Linear
B) Tetrahedral
C) Trigonal planar
D) Octahedral
Answer: Trigonal planar

10. Carbonyl compounds have higher boiling points than comparable alkanes due to:
A) Hydrogen bonding between molecules
B) Dipole-dipole interactions
C) Covalent bonding
D) London dispersion forces only
Answer: Dipole-dipole interactions

11. Why do carbonyl compounds have lower boiling points than comparable alcohols?
A) They have higher molecular weight
B) They cannot form intermolecular hydrogen bonds with each other
C) They are less polar
D) They have weaker dipole-dipole interactions
Answer: They cannot form intermolecular hydrogen bonds with each other

12. Lower members of aldehydes and ketones (up to C_4) are soluble in water because:

Periodic Classification of Elements and Atomic Structure

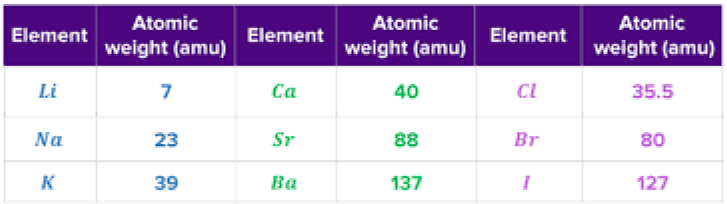
Historical Development of the Periodic Table

Early Attempts at Classification

Al-Razi: Classified substances based on their physical and chemical properties.

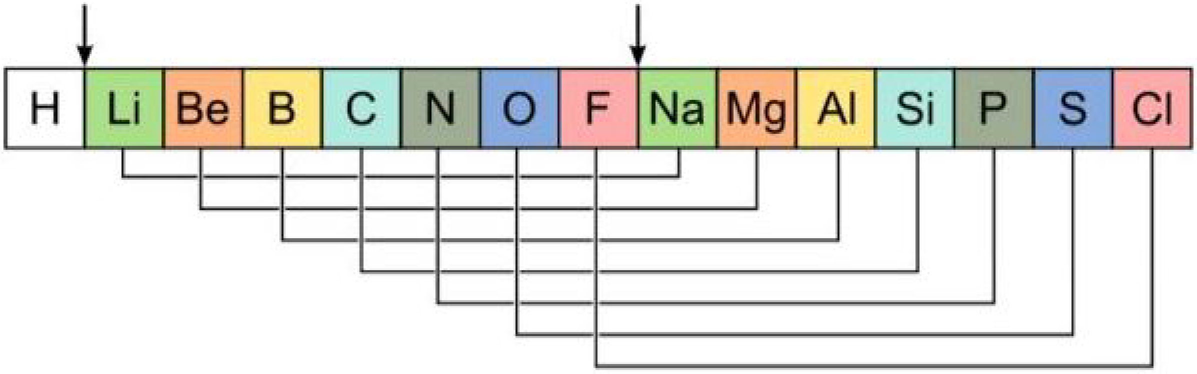
Dobereiner's Triads (1829): Grouped elements into triads (groups of three) with similar properties. The atomic mass of the middle element was roughly the average of the other two.

Newlands' Law of Octaves (1864): Noted that when elements were arranged by increasing atomic mass, every eighth element had similar properties, like the octaves in music.



Element	Atomic weight (amu)	Element	Atomic weight (amu)	Element	Atomic weight (amu)
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

Table: Dobereiner's traids



Mendeleev's Periodic Table (1871)

Basis: Arranged elements in ascending order of their **atomic masses**.

Structure: Presented a regular table with vertical columns called **Groups** and horizontal rows called **Periods**.

Mendeleev's Periodic Law:

'The properties of elements are a periodic function of their atomic masses'.

Achievements:

Successfully predicted the existence and properties of undiscovered elements (e.g., Gallium, Germanium) by leaving gaps in his table.

The accuracy of these predictions led to the widespread acceptance of his periodic table.

Special Family Names

Group 1 (IA): Alkali Metals

Group 2 (IIA): Alkaline Earth Metals

Group 17 (VIIA): Halogens

Group 18 (VIIIA): Noble Gases

Metals, Non-Metals, and Metalloids

Metals: Located on the left-hand side and center of the table. They are lustrous, malleable, ductile, and good conductors of heat and electricity. They form cations and basic oxides.

Non-Metals: Located on the top right-hand side (above the stepped line). They are generally poor conductors and form anions and acidic oxides.

Metalloids (Semi-metals): Elements bordering the stepped line (e.g., B, Si, Ge, As, Sb, Te) that have properties intermediate between metals and non-metals.

Periodic Trends in Physical Properties

Atomic Size (Atomic Radius)

It has two types

(1) Covalent radius: half the distance between nuclei of two covalently bonded identical atoms.

(2) **Van der Waals radius**: for non-bonded atoms;

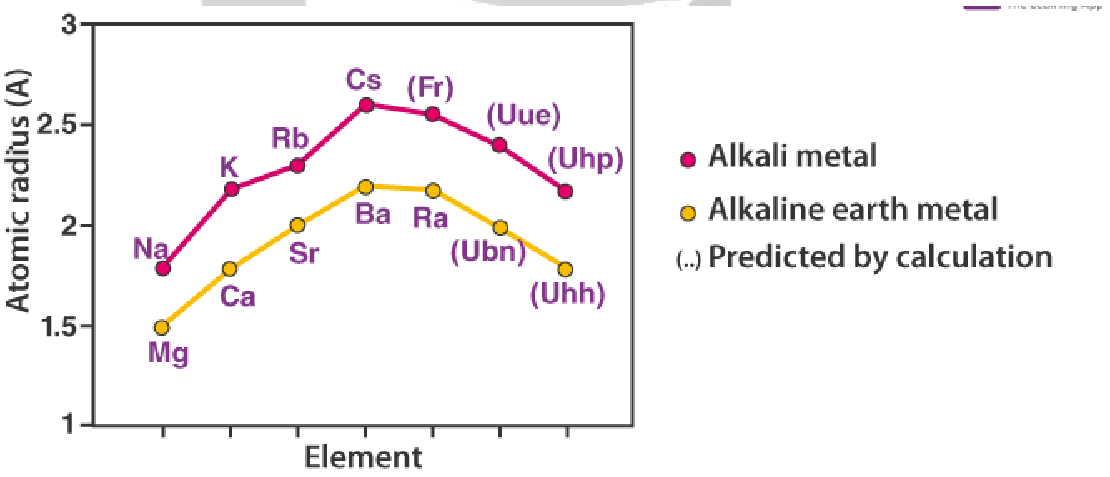
Trend Across a Period (Left to Right): Decreases.

Reason: Z_{eff} increases significantly, pulling the valence electrons closer to the nucleus. The shielding effect remains almost constant.

Trend Down a Group (Top to Bottom): Increases.

Reason: The principal quantum number n increases, adding a new electron shell farther from the nucleus. This outweighs the increase in Z_{eff}.

Ionic Radius



Cation than parent atoms because: (a) electron(s) removed from valence shell; (b) reduced electron-electron repulsion; (c) increased effective nuclear charge per remaining electron.

Anions: Larger than their parent atoms because the added electron(s) increase electron-electron repulsion, causing the electron cloud to expand.

Isoelectronic Ions: Ions with the same number of electrons. Size decreases with increasing nuclear charge (e.g., $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$).

Ionization Energy (I.E.)

Definition: The minimum energy required to remove the most loosely bound electron from an isolated gaseous atom in its ground state.

$X(g) \rightarrow X^+(g) + e^-$ (First I.E.)

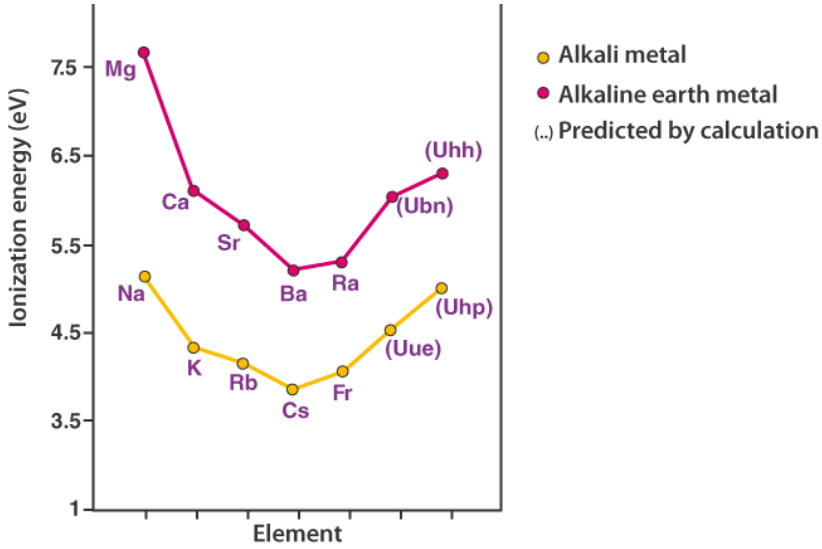
Trend across a Period: Trend Across a Period: Generally increases from left to right, with notable exceptions between Groups 2 & 13 and 15 & 16 due to stability of fully/half-filled subshells and electron-electron repulsion.

Reason: Decreasing atomic size and increasing Z_{eff}. Make it harder to remove an electron

.

Trend Down a Group: Decreases.

Reason: Increasing atomic size and shielding effect make it easier to remove an electron.



Exceptions: Slight drops are observed between Group 2 and 13 (e.g., Be to B) due to the removal of a p electron instead of an s electron, and between Group 15 and 16 (e.g., N to O) due to increased repulsion when pairing electrons in p orbitals.

Electron Affinity (E.A.)

Definition: The energy change when an electron is added to an isolated gaseous atom to form a negative ion.

$X(g) + e^- \rightarrow X^-(g)$ (First E.A.)

A more negative E.A. means a greater tendency to accept an electron.

Trend Across a Period: Becomes more negative (increases).

Reason: Decreasing atomic size and increasing Z_{eff} make it easier to add an electron.

Trend Down a Group: Becomes less negative (decreases).

Reason: Increasing atomic size makes it harder to add an electron.

Note: The second E.A. is always positive (endothermic) because energy is required to add an electron to a negatively charged ion.

Electronegativity

Definition: The ability of an atom in a molecule to attract the shared pair of electrons towards itself.

Trend across a Period: Increases.

Trend down a Group: Decreases.

Application: Used to predict bond type.

ΔEN > 1.8: Ionic Bond

ΔEN 0.4 to 1.8: Polar Covalent Bond

ΔEN < 0.4: Non-Polar Covalent Bond

Metallic and Non-Metallic Character

Metallic Character: The tendency of an atom to lose electrons and form positive ions.

Trend across a Period: Decreases.

Trend down a Group: Increases.

Non-Metallic Character: The tendency of an atom to gain electrons and form negative ions.

Trend across a Period: Increases.

Trend down a Group: Decreases.

Melting and Boiling Points

Across a Period (s- and p-blocks): Increase to a maximum around Group 14 (due to strong covalent network bonding, e.g., Carbon as diamond) and then decrease sharply to the noble gases (which have weak London dispersion forces).

Down a Group (Metals, e.g., IA, IIA): Generally decrease due to weaker metallic bonding as atomic size increases.

Down a Group (Molecular Non-Metals, e.g., VIIA): Increase due to increasing molecular size and stronger London dispersion forces.

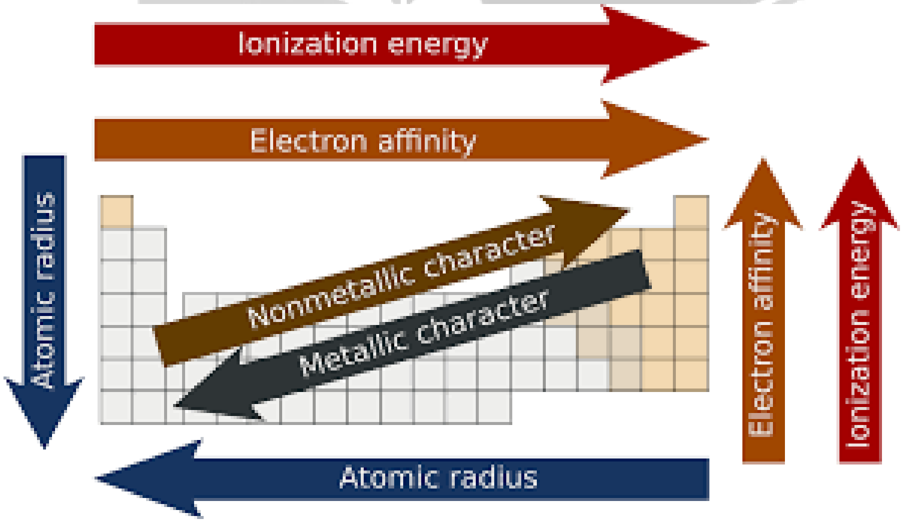


Fig. General trend In one frame

Periodicity in Compounds

Hydrides

Binary compounds of hydrogen.

Ionic (Saline) Hydrides: Formed by s-block elements except Be and partially except Mg (BeH_2 is covalent polymeric; MgH_2 is intermediate).

Topic-wise One-Liner on Periodic Classification of Elements & Atomic Structure

1. Historical Development of the Periodic Table

1. **Al-Razi** classified substances based on their physical and chemical properties.
2. **Dobereiner** grouped elements into **triads** where the atomic mass of the middle element was approximately the average of the other two.
3. **Newlands** proposed the **Law of Octaves**, stating that every eighth element had similar properties when arranged by atomic mass.
4. **Mendeleev** created the first successful periodic table based on **atomic masses**.
5. Mendeleev's **Periodic Law** states that the properties of elements are a periodic function of their atomic masses.
6. A major achievement of Mendeleev's table was the correct **prediction of the properties of undiscovered elements** like Gallium and Germanium.
7. The modern periodic table is based on **atomic number**, as established by **Henry Moseley**.
8. The **Modern Periodic Law** states that the properties of elements are a periodic function of their atomic numbers.
9. The modern table rectifies the position of **isotopes** as they have the same atomic number.
10. The **noble gases** (Group 18) were a new addition to the modern periodic table.

2. Structure of the Modern Periodic Table

11. **Groups** are the vertical columns in the periodic table, and elements in the same group have the same number of **valence electrons**.
12. **Periods** are the horizontal rows, and the period number signifies the **highest principal quantum number (n)**.
13. Based on the subshell being filled, elements are classified into **s, p, d, and f blocks**.
14. **s-block elements** have valence electrons in the s-orbital and include **Groups 1 and 2** (Alkali and Alkaline Earth Metals).
15. **p-block elements** have valence electrons in the p-orbital and include **Groups 13 to 18**.
16. **d-block elements** d-block elements (Groups 3-12) where differentiating electron enters d-orbital. Transition elements are d-block elements that form at least one ion with partially filled d-orbital. Group 12 (Zn, Cd, Hg) are not -Typical transition elements (full d^{10} in ground and common oxidation states)
17. **f-block elements** have valence electrons in the f-orbital and are called **Inner Transition Elements** (Lanthanides and Actinides).
18. **Group 1** elements are called **Alkali Metals**.
19. **Group 2** elements are called **Alkaline Earth Metals**.
20. **Group 17** elements are called **Halogens**.
21. **Group 18** elements are called **Noble Gases**.
22. **Metals** are located on the left and center of the table, are lustrous, malleable, and form **cations** and **basic oxides**.
23. **Non-metals** are located on the top right, are generally poor conductors, and form **anions** and **acidic oxides**.
24. **Metalloids** (e.g., B, Si, Ge) have properties intermediate between metals and non-metals.

Practice MCQs

1. Elements are arranged in the periodic table in order of increasing:

A) Atomic mass

B) Atomic number

C) Number of neutrons

D) Number of shells

Answer: Atomic number

2. The number of valence electrons in an element of group 13 is:

A) 1

B) 3

C) 5

D) 7

Answer: 3

3. Which period contains the element with electronic configuration 2,8,8,2?

A) 2

B) 3

C) 4

D) 5

Answer: 4

4. As we move from top to bottom in a group, the atomic radius generally:

A) Decreases

B) Increases

C) Remains constant

D) First decreases then increases

Answer: Increases

5. The screening effect increases down a group because of:

A) Increase in number of shells

B) Decrease in nuclear charge

C) Increase in valence electrons

D) Decrease in atomic size

Answer: Increase in number of shells

6. Which element has the highest melting point in period 2?

A) Lithium

B) Carbon

C) Nitrogen

D) Fluorine

Answer: Carbon

7. In period 3, the element with the highest melting point is:

A) Sodium

B) Magnesium

C) Aluminum

D) Silicon

Answer: Silicon

8. Which group elements are known as coinage metals?

A) IA

B) IIA

C) IB

D) VIIA

Answer: IB

9. The best conductor of electricity among the following is:

A) Sodium

B) Magnesium

C) Aluminum

D) Silicon

Answer: Aluminum

10. Which of the following has the smallest atomic radius?

A) Na^+

B) Mg^{2+}

C) Al^{3+}

D) Si^{4+}

Answer: Si^{4+}

11. Ionization energy is lowest for:

A) Alkali metals

B) Halogens

C) Noble gases

D) Transition metals

Answer: Alkali metals

12. Nitrogen has higher ionization energy than oxygen due to:

A) Smaller atomic size

B) Greater nuclear charge

S and P-Block Elements

Elements are classified into blocks based on the type of atomic orbital in which the valence electrons reside.

Block	Valence Orbital	General Electronic Configuration	Groups Included
s-Block	s-orbital	ns^{1-2}	IA (Alkali metals), IIA (Alkaline earth metals), and Helium
p-Block	p-orbital	$ns^2 np^{1-6}$	IIIA to VIIIA (Noble gases), except Helium
d-Block	d-orbital	$ns^2 (n-1)d^{1-10}$	Transition elements (Group IIIB to VIIIB, IB, IIB)
f-Block	f-orbital	$(n-2)f^{1-14} (n-1) d^{0\text{-}1} ns^2$	Lanthanides and Actinides

General Properties of S-Block Elements

. **Physical Properties**

Appearance: Soft, silvery-white, lustrous metals (except Lithium turns grey in air).

Density & Melting/Boiling Points: Density generally increases down the group, **although** irregularly (e.g., Mg > Ca) low melting, and boiling points (Alkali metals are softer than Alkaline Earth metals).

Conductivity: Excellent conductors of heat and electricity.

Flame Colors: Impart characteristic colors to flames **(e.g. Li: Red, Na: Yellow, K: Violet**).

Chemical Properties

Valence Electrons: Have 1 (Group 1) or 2 (Group 2) electrons in their outermost *s*-orbital, with general configuration ns^1 **or** ns^2.

Ionization Energy: Very low ionization enthalpies, making them highly electropositive.

Reactivity: Highly reactive; reactivity increases down the group, typically stored in oil (except Be, Mg).

Ion Formation: Easily lose valence electrons to form +1 (Group 1) or +2 (Group 2) ions (cations).

Compound Nature: Form predominantly ionic compounds. Covalent character is observed in compounds of small cations with high charge density (e.g., $BeCl_2$ is covalent; LiCl, $MgCl_2$ show some covalent character)

Oxides: Form basic oxides and hydroxides (e.g., M_2O, MO), which react with water to form strong bases (alkalies).

Reducing Agents: Act as strong reducing agents.

Group IA: Alkali Metals

Elements: Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs), Francium (Fr).

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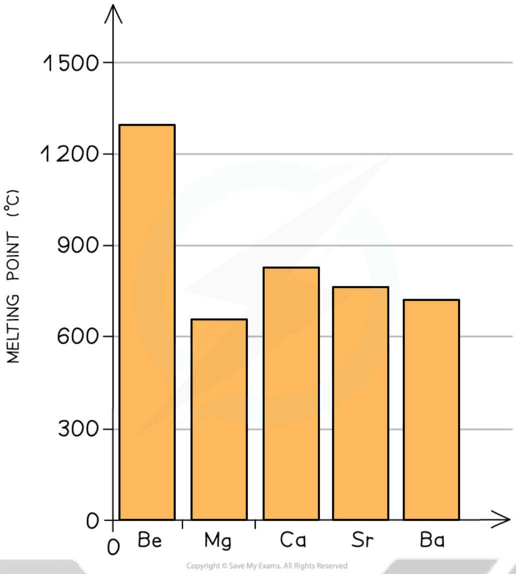


M.P of alkaline Earth elements

Important Reactions of Alkaline Earth Metals

Reaction with Oxygen: Form monoxides (MO).

Beryllium oxide (BeO) is **amphoteric**.

Other oxides (MgO CaO etc.) are **basic**. Their basicity increases down the group.

Barium also forms a peroxide (BaO_2) at high temperatures.

Reaction with Water:

Beryllium (Be): No reaction.

Magnesium (Mg): Reacts with hot water or steam.

$Mg+2H_2O \rightarrow Mg(OH)_2$ (hot water)

$Mg+H_2O \rightarrow MgO+H_2$ (steam)

Calcium (Ca), Strontium (Sr), Barium (Ba): React with cold water to form hydroxides and hydrogen.

Reaction with Nitrogen: Form nitrides (M_3N_2).

$3M+N_2 \rightarrow M_3N_2$

These nitrides react with water to produce ammonia.

$Ca_3N_2+6H_2O \rightarrow 3Ca(OH)_2+2NH_3$

Solubility Trends

Hydroxides [M (OH) $_2$]: Solubility in water **increases** down the group. Be (OH) $_2$ insoluble, Ba (OH)2 is highly soluble.

Sulphates (MSO$_4$: Solubility in water **decreases** down the group. $BeSO_4$ and $MgSO_4$ are soluble, $BaSO_4$is highly insoluble.

P-Block Elements

Group IIIA Elements

General Configuration: ns^2np^1

Elements: Boron (B), Aluminium (Al), Gallium (Ga), Indium (In), Thallium (Tl).

Trend: Metallic character increases down the group. Boron is a non-metal, Aluminium is a metal, and the rest are metals with increasing metallic character.

Topic-Wise One-Liners: s and p-Block Elements

1. The Periodic Table and Periodicity

1. The **Modern Periodic Table** is arranged based on increasing **atomic number**.
2. For s- and p-block elements, the **group number** In **A-group notation**, group number equals valence electrons; in modern IUPAC groups 13–18, valence electrons = (group no. − 10).”
3. The **period number** indicates the total number of **electron shells** in an atom.
4. **Valence electrons** are the electrons in the outermost shell and determine an element's chemical properties.
5. **Metals** typically have 1-3 valence electrons and tend to lose electrons to form **cations**.
6. **Non-metals** typically have 4-7 valence electrons and tend to gain electrons to form **anions**.
7. **Metalloids** (e.g., B, Si, Ge) exhibit properties of both metals and non-metals.
8. **Noble gases** have a completely filled valence shell and are chemically very unreactive.
9. Elements are classified into **s, p, d, and f blocks** based on the orbital where the valence electrons reside.
10. The general electronic configuration for the **s-block** is ns^{1-2}.
11. The general electronic configuration for the **p-block** is $ns^2 np^{1-6}$.

2. Periodic Trends in Physical Properties

Trends Down a Group:

12. **Atomic/Ionic radius increases** down a group due to an increase in the number of electron shells.
13. **Ionization Energy (IE) decreases** down a group due to increased atomic size and the shielding effect.
14. **Electron Affinity (EA) decreases** down a group due to increased atomic size and shielding.
15. An exception to the EA trend is that **Chlorine has a higher electron affinity than Fluorine**.
16. **Electronegativity (EN) decreases** down a group.
17. **Metallic character increases** down a group.
18. **Electropositive character increases** down a group.

Trends Across a Period:

19. **Atomic radius decreases** across a period due to an increase in effective nuclear charge.
20. **Ionization Energy (IE) increases** across a period due to decreasing atomic radius.
21. An exception to the IE trend is that **Nitrogen has a higher IE than Oxygen** due to its stable half-filled p-subshell.
22. **Electron Affinity (EA) increases** across a period.
23. **Electronegativity (EN) increases** across a period.
24. **Metallic character decreases** across a period.
25. **Electropositive character decreases** across a period.

Melting & Boiling Points:

26. Across a period (e.g., Period 2 & 3), m.p. and b.p. **increase from Group IA to IVA** due to stronger bonding.
27. From Group VA to VIIIA, m.p. and b.p. **decrease sharply** as elements form small molecules with weak intermolecular forces.
28. Down a group of **metals**, m.p. and b.p. **decrease** due to weaker metallic bonding.
29. Down a group of **non-metals**, m.p. and b.p. **increase** due to stronger London dispersion forces.

Practice MCQs

1. Which one of the following is the least basic in nature?

A) NF_3

B) NCl_3

C) NBr_3

D) NI_3

Answer: NF_3

2. The oxide of nitrogen which causes hysterical laughter is:

A) N_2O_3

B) NO_2

C) N_2O

D) NO

Answer: N_2O

3. The basicity of orthophosphoric acid (H_3PO_4) is:

A) 1

B) 2

C) 3

D) 4

Answer: 3

4. Bone ash contains calcium phosphate approximately:

A) 40%

B) 50%

C) 70%

D) 80%

Answer: 80%

5. In the Contact Process, arsenic impurities are removed:

A) by prolong heating the gases

B) by treating with $Fe(OH)_3$

C) in the scrubbing tower

D) in the absorption tower

Answer: by treating with $Fe(OH)_3$

6. Which of the following acids possesses oxidizing and reducing properties?

A) HCl

B) HNO_2

C) HNO_3

D) H_2SO_4

Answer: HNO_2

7. Sugar becomes black when concentrated H_2SO_4 is added due to:

A) Hydrolysis

B) Hydration

C) Dehydration

D) Decolourization

Answer: Dehydration

8. SO_3 is not absorbed directly in water to form H_2SO_4 because:

A) The reaction does not go to completion

B) The reaction is quite slow

C) The reaction is highly exothermic

D) SO_3 is insoluble in water

Answer: The reaction is highly exothermic

9. Nitric acid behaves as an oxidizing agent in its reaction with:

A) Ammonia

B) Sodium hydroxide

C) Copper

D) Sodium carbonate

Answer: Copper

10. Which of the following oxyacids has reducing power?

A) H_3PO_3

B) H_3PO_4

C) $H_4P_2O_7$

D) All of these

Answer: H_3PO_3

11. Fuming nitric acid contains an excess of:

A) N_2O_5

B) NO_2

C) NO

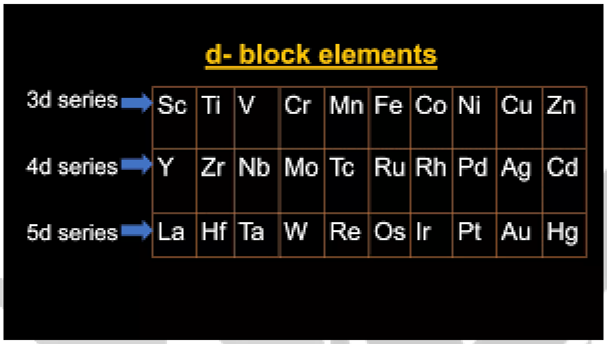
Transition Elements (d-Block) & Coordination Chemistry

Introduction to Transition Elements

Definition:

Transition elements are defined as those elements which have incompletely filled **d-orbitals** in their ground state or in any of their common oxidation states. The f-block elements (Lanthanides and Actinides) are often called **Inner Transition Elements** and have incompletely filled f-orbitals.

Location in the Periodic Table:



d- block elements

3d series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4d series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5d series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

They are located in the central part of the periodic table, spanning **Groups 3 to 12**, positioned between the electropositive s-block metals and the electronegative p-block elements.

Electronic Configuration

General Valence Shell Configuration:

The general electronic configuration for d-block elements is **(n-1) d^{1-10} ns^{1-2}** with exceptions **(Cr, Cu, Mo, Ag, Au, Pd)**

First Transition Series (3d): Scandium (Sc, 21) to Zinc (Zn, 30)

Second Transition Series (4d): Yttrium (Y, 39) to Cadmium (Cd, 48)

Third Transition Series (5d): Lanthanum (La, 57), Hafnium (Hf, 72) to Mercury (Hg, 80)

Fourth Transition Series (6d): Actinium (Ac, 89), Rutherfordium (Rf, 104) onwards (incomplete and radioactive).

Exceptions to the Aufbau Principle:

Certain elements deviate from the expected order of filling to achieve extra stability.

1. **Chromium (Cr, 24):** Expected: [Ar] $3d^4$ $4s^2$ | **Actual: [Ar] $3d^5$ $4s^1$**
2. **Copper (Cu, 29):** Expected: [Ar] $3d^9$ $4s^2$ | **Actual: [Ar] $3d^{10}$ $4s^1$**
3. **Other Examples:** Molybdenum (Mo, 42), Silver (Ag, 47), and Gold (Au, 79) show similar behavior.

Reason for Exceptions: Atoms gain extra stability from a **half-filled (d^5)** or **fully filled (d^{10})** d-subshell. This configuration leads to symmetrical electron distribution and minimized electron-electron repulsion, making it more energetically favorable.

Classification: Typical vs. Non-Typical Transition Elements

Typical Transition Elements: Elements from Groups 4 to 11 (e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu). They exhibit characteristic properties like variable oxidation states, colored ions, and catalytic activity.

Topic Wise One Liners on Transition elements and Coordination Chemistry:

1. **Transition elements** are defined as those elements which have incompletely filled **d-orbitals** in their ground state or in any of their common oxidation states.
2. The general electronic configuration of transition elements is **$(n\text{-}1)d^{1-10}\ ns^{1-2}$**.
3. Zinc (Zn), Cadmium (Cd), and Mercury (Hg) are not considered typical transition elements as their d-subshell is completely filled.
4. Transition elements are characterized by **variable oxidation states**, **complex formation**, and **colored ions**.
5. Not all ions of transition elements are colored; for example, Sc^{3+} and Zn^{2+} are colorless due to empty and fully filled d-orbitals, respectively.
6. Transition elements can form **interstitial compounds** when small non-metal atoms like H, B, C, or N occupy the empty spaces in their crystal lattices.
7. The formation of interstitial compounds makes the parent metal **more brittle** and **harder**.
8. **Non-stoichiometric compounds** are those that do not obey the law of definite proportions and are often **interstitial compounds**.
9. Transition elements and their compounds often act as good **catalysts** due to their variable oxidation states.
10. Negative oxidation states are shown by transition elements in **complexes** and **carbonyls**.

2. Electronic Configurations and Paramagnetism

11. The electronic configuration of Chromium (Cr, Z=24) is **$3d^5\ 4s^1$**, not $3d^4\ 4s^2$, due to the extra stability of a half-filled d-subshell.

12. The number of **unpaired electrons** in an atom or ion determines its **paramagnetic character**.

13. The ion with the maximum number of unpaired electrons will exhibit the **maximum paramagnetic character**.

14. Mn^{2+} ion has the electronic configuration [Ar] $3d^5$, meaning it has **5 unpaired electrons**.

15. Fe^{3+} ion has the electronic configuration [Ar] $3d^5$, meaning it also has **5 unpaired electrons**.

16. Cu^{2+} ion has the electronic configuration [Ar] $3d^9$, meaning it has only **1 unpaired electron**.

17. The **least paramagnetism** is shown by ions with the fewest or zero unpaired electrons, such as Cu^{2+}.

18. Along a period in the transition series, the **paramagnetic character** first increases to a maximum and then decreases.

19. Along a period, the **covalent radii** of transition elements in their ionic state generally **decrease**.

3. Coordination Chemistry

20. A **coordination compound** consists of a central metal atom or ion surrounded by ligands.

21. The **coordination sphere** refers to the central metal ion and the ligands attached to it.

22. The **coordination number** is the total number of coordinate bonds formed between the central metal ion and the ligands.

23. In the complex $[Ag(NH_3)_2]^+$, the coordination number of Silver (Ag) is **2**.

24. In the complex $[PtCl(NO_2)(NH_3)_4]^{2+}$, the coordination number of Platinum (Pt) is **6**.

25. **Ligands** are ions or molecules that donate a pair of electrons to the central metal atom.

26. **Monodentate ligands** donate

Practice MCQs

1. Which of the following is a defining characteristic of transition metals according to the broader definition used in the text?

A) They always have partly filled d or f shells as neutral atoms.

B) They have partly filled d or f shells in any commonly occurring oxidation state.

C) They are all non-metals.

D) They do not form colored ions.

Answer: They have partly filled d or f shells in any commonly occurring oxidation state.

2. The element scandium is considered the lightest member of which series?

A) First transition series

B) Second transition series

C) Lanthanide series

D) Actinide series

Answer: First transition series

3. Why are the chemical properties of the lanthanides so homogeneous compared to the d-block elements?

A) Their 4f orbitals are exposed and interact strongly with the environment.

B) Their 4f orbitals are deeply buried and shielded from the surroundings.

C) They have variable oxidation states.

D) They form primarily covalent bonds.

Answer: Their 4f orbitals are deeply buried and shielded from the surroundings.

4. Which of the following oxidation states is maximum in 3d series and has no physical reality as a simple ion?

A) Ti^{3+}

B) Mn^{7+} in MnO_4^-

C) Fe^{2+}

D) Cu^{2+}

Answer: Mn^{7+} in MnO_4^-

5. In the first transition series, the highest oxidation state is NOT exhibited by which element in stable compounds?

A) Scandium

B) Chromium

C) Manganese

D) Iron

Answer: Iron

6. According to the 18-electron rule, the homoleptic carbonyl with the formula $V(CO)_6$ is an exception because it has:

A) 16 electrons

B) 17 electrons

C) 18 electrons

D) 20 electrons

Answer: 17 electrons

7. The synergic bonding in metal carbonyls involves:

A) Only σ donation from CO to the metal.

B) Only π back-donation from the metal to CO.

C) Both σ donation from CO and π back-donation from the metal.

D) Neither σ nor π bonding.

Answer: Both σ donation from CO and π back-donation from the metal.

8. What physical evidence strongly supports the existence of M--CO π back-bonding?

A) Increase in C--O bond length and decrease in M--C bond length.

B) Decrease in both C--O and M--C bond lengths.

C) Increase in C--O stretching frequency.

D) Decrease in the metal's oxidation state.

Answer: Increase in C--O bond length and decrease in M--C bond length.

9. When CO groups in a metal carbonyl are replaced by ligands with poor π-acceptor ability, the stretching frequencies of the remaining CO groups typically:

A) Increase.

B) Decrease.

C) Remain the same.

D) Become zero.

Answer: Decrease.

Stoichiometry

Atomic Structure & Basic Concepts

Atom

An **atom** is the smallest particle of an element that can take part in a chemical reaction. It retains the chemical properties of that element.

- **Historical Background**:
  Ancient Greek philosophers (like Democritus) proposed the idea of **"atomos"** (indivisible particles).
  John Dalton (1808) formulated the **atomic theory**, explaining laws of conservation of mass and definite proportions.
- **Modern View**: Atoms consist of subatomic particles: **electrons, protons, neutrons** (fundamental particles), and others like neutrinos.

Molecule

A **molecule** is the smallest particle of a pure substance that can exist independently.

- **Atomicity**: Number of atoms in a molecule.
  Monoatomic: He, Ne
  Diatomic: O_2, Cl_2
  Polyatomic: O_3, P_4, S_8
- **Macromolecules**: Very large molecules (e.g., haemoglobin → 10,000 atoms).

Ion

Ions are charged species formed by loss or gain of electrons.

- **Cation**: Positively charged ion (e.g., Na^+, Ca^{2+}, Al^{3+}) → formed by loss of electrons (endothermic process).
- **Anion**: Negatively charged ion (e.g., Cl^-, S^{2-}, SO_4^{2-}) → formed by gain of electrons (exothermic process up to uninegative ion).
- **Molecular Ions**: CH_4^+, CO^+, N_2^+ (formed by ionization of molecules).

Relative Atomic Mass & Isotopes

Relative Atomic Mass (RAM)

RAM is the mass of an atom compared to 1/12th of the mass of a carbon-12 atom.

- Unit: **Atomic Mass Unit (amu)** = 1.661×10^{-27} kg1.661×10^{-27kg}.
- Example: RAM of H = 1.008 amu, O = 15.9994 amu.

Isotopes

Isotopes are atoms of the same element with same atomic number but different mass numbers (due to different neutrons).

- **Examples**:
  Carbon: $_{12}C$, $_{13}C$, $_{14}C$
  Hydrogen: Protium ($_1H$), Deuterium ($_2H$), Tritium ($_3H$)
- **Natural Abundance**: Determined by **mass spectrometry**.

Topic Wise One Liners: Stoichiometry

1. ATOMIC STRUCTURE & BASIC CONCEPTS

1. An **atom** is the smallest particle of an element that can take part in a chemical reaction and retains its chemical properties.
2. The modern atomic model consists of subatomic particles: **electrons, protons, and neutrons**.
3. A **molecule** is the smallest particle of a pure substance that can exist independently.
4. **Atomicity** refers to the number of atoms in a molecule (e.g., monoatomic He, diatomic O_2, polyatomic O_3).
5. **Ions** are charged species formed by the loss or gain of electrons.
6. A **cation** is a positively charged ion (e.g., Na^+) formed by the loss of electrons, which is an **endothermic process**.
7. An **anion** is a negatively charged ion (e.g., Cl^-) formed by the gain of electrons, which is an **exothermic process**.
8. **Molecular ions** are ions formed from molecules, e.g., CH_4^+, CO^+.

2. RELATIVE ATOMIC MASS & ISOTOPES

9. **Relative Atomic Mass (RAM)** is the mass of an atom compared to 1/12th the mass of a carbon-12 atom.

10. The unit of RAM is the **Atomic Mass Unit (amu)**, where 1 amu = 1.661×10^{-27} kg.

11. **Isotopes** are atoms of the same element with the same atomic number but different mass numbers due to different numbers of neutrons.

12. **Average atomic mass** is calculated from the isotopic masses and their natural abundances: Σ(isotopic mass × % abundance)/100.

13. **Mass spectrometry** is used to determine the natural abundance of isotopes.

3. EMPIRICAL & MOLECULAR FORMULAS

14. **Percentage composition** of an element in a compound is calculated as: (Mass of element in compound / Mass of compound) × 100.

15. The **empirical formula** gives the simplest whole-number ratio of atoms in a compound.

16. Steps to find the empirical formula: Find % composition, convert to moles, find mole ratio, convert to simplest whole numbers.

17. The **molecular formula** gives the actual number of atoms in a molecule.

18. Molecular formula = n × (Empirical formula), where n = Molecular mass / Empirical formula mass.

19. **Gram atomic mass** is the relative atomic mass expressed in grams; it contains one mole of atoms.

4. THE MOLE CONCEPT & AVOGADRO'S NUMBER

20. A **mole** is the amount of substance that contains **6.022×10^{23}** particles (atoms, molecules, ions, etc.), known as **Avogadro's number (N_a)**.

21. **Molar mass** is the mass of one mole of a substance in g/mol.

Practice MCQs

1. An atom is the smallest particle of an element that retains its chemical properties and can participate in a chemical reaction.
A. True
B. False
C. Only for metals
D. Only for non-metals
Correct Answer: (A)

2. The subatomic particles that constitute an atom are:
A. Electrons and protons only
B. Protons and neutrons only
C. Electrons, protons, and neutrons
D. Positrons and neutrinos
Correct Answer: (C)

3. A molecule that consists of only one atom is called:
A. Diatomic
B. Polyatomic
C. Monoatomic
D. Macromolecule
Correct Answer: (C)

4. An ion formed by the loss of electrons is called a:
A. Anion
B. Cation
C. Molecular ion
D. Neutral atom
Correct Answer: (B)

5. The formation of an anion is generally an:
A. Endothermic process
B. Exothermic process
C. Isothermal process
D. Adiabatic process
Correct Answer: (B)

6. Relative Atomic Mass (RAM) is expressed in units of:
A. Grams
B. Kilograms
C. Atomic Mass Unit (amu)
D. Moles
Correct Answer: (C)

7. Isotopes of an element have the same number of:
A. Neutrons
B. Mass number
C. Atomic number
D. Nucleons
Correct Answer: (C)

8. The average atomic mass of neon (90.92% ^{20}Ne, 0.26% ^{21}Ne, 8.82% ^{22}Ne) is approximately:
A. 20.18 amu
B. 20.00 amu
C. 21.00 amu
D. 22.00 amu
Correct Answer: (A)

9. The empirical formula of a compound shows the:
A. Actual number of atoms
B. Simplest whole-number ratio of atoms
C. Molecular geometry
D. Type of bonding
Correct Answer: (B)

10. If the empirical formula is CH_2O and the molecular mass is 180, the molecular formula is:
A. $C_3H_6O_3$
B. $C_6H_{12}O_6$
C. $C_2H_4O_2$
D. $C_5H_{10}O_5$
Correct Answer: (B)

11. One mole of any substance contains:
A. 6.022×10^{22} particles
B. 6.022×10^{23} particles
C. 22.4 particles
D. 1 gram of the substance
Correct Answer: (B)

12. The number of moles in 60g of NaOH (molar mass 40 g/mol) is:
A. 1.0 mol
B. 1.5 mol

Atomic Structure

Historical Development of the Atomic Theory

Early Greek Philosophers and the Concept of the Atom

Leucippus (500 B.C): First proposed that matter is composed of indivisible particles. He is known as the father of atomic philosophy.

Democritus (430 B.C): A student of Leucippus, he named these fundamental particles "atomos," meaning "uncuttable" or "indivisible."

He theorized that different properties of matter (e.g., sour taste, white color) arose from the different shapes and sizes of these atoms.

He believed changes in matter were due to the combination and separation of atoms.

Dalton's Atomic Theory (1808)

John Dalton converted the philosophical idea of the atom into a scientific theory based on experimental evidence.

Main Postulates:

- Matter is composed of indivisible atoms.
- Atoms of the same element are identical in mass and properties. Compounds are formed by the combination of atoms of different elements in simple whole-number ratios.
- Chemical reactions involve the rearrangement of atoms.
- **Significance:** This theory laid the experimental foundation for modern chemistry.

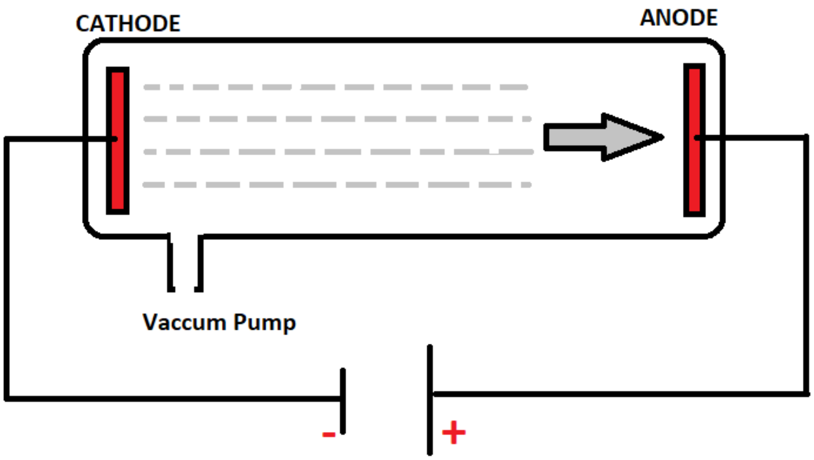
Discovery of Subatomic Particles

The indivisibility of the atom was challenged by the discovery of subatomic particles.

Discovery of the Electron (Cathode Rays)

Experiment: Sir William Crookes and J.J. Thomson used a **gas discharge tube** at low pressure (~0.01 mm Hg) with a high voltage (5000-10,000 V).

Observations: Rays originated from the cathode (negative electrode) and traveled towards the anode, causing fluorescence on the glass wall opposite the cathode.



These were named **cathode rays**.

Properties of Cathode Rays (J.J. Thomson's Conclusions):

Travel in straight lines from the cathode, casting sharp shadows.

Are negatively charged (deflected towards the positive plate in an electric field).

Are deflected by a magnetic field.

Possess momentum and kinetic energy (can rotate a paddle wheel).

Their e/m (charge-to-mass ratio) is constant (**1.7588×10^{11} C/kg**), regardless of the gas or electrode material in the tube.

Can produce X-rays upon striking a metal anode.

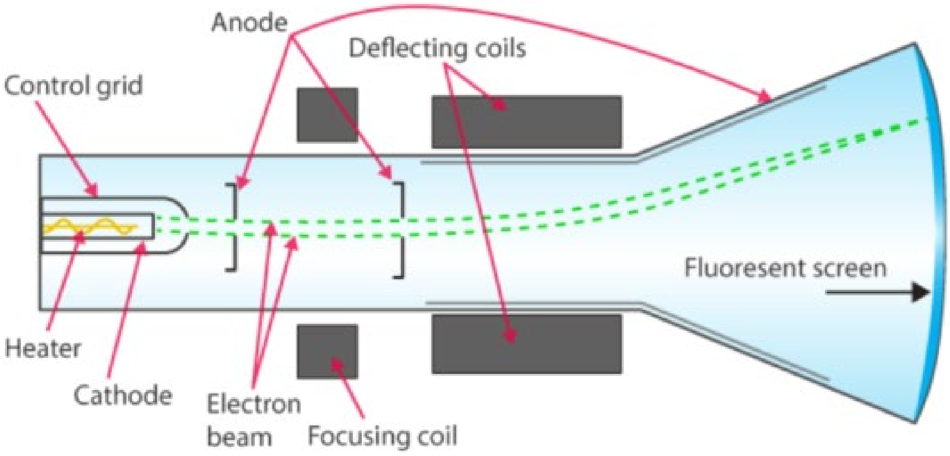
Conclusion (J.J. Thomson): Cathode rays are streams of negatively charged particles, which were later named **electrons** by Stoney. All atoms contain electrons.

Discovery of the Proton (Positive Rays / Canal Rays)

Experiment: Eugene Goldstein (1886) used a perforated cathode in a discharge tube.

Observations: Along with cathode rays moving away from the cathode, new rays were observed moving *towards* the cathode and passing through its holes (canals). These were called **canal rays** or **positive rays**.

Reason for Production: High-speed electrons (cathode rays) collide with gas molecules, knocking out electrons and creating positive ions **$M + e^-$ (high-speed) $\rightarrow M^+ + e^-$ (slow) $+ e^-$ (knocked-out)** these positive ions are attracted to the cathode.



Properties of Positive Rays:

Travel in straight lines.

Are positively charged (deflected towards the negative plate in an electric field).

Are deflected by a magnetic field in the opposite direction to electrons.

The e/m value depends on the nature of the gas in the tube.

The maximum e/m value is observed when hydrogen gas is used. This lightest positive particle was named the **proton**.

Discovery of the Neutron

Experiment: James Chadwick (1932) bombarded a beryllium ($^{9}_{4}Be$) target with alpha (α) particles from polonium.

Finding: The charge on the droplets was always an integral multiple of (1.59$\times 10^{-19}$ which is close to modern value of 1.6022×10^{-19} C, which is the **charge of a single electron**.

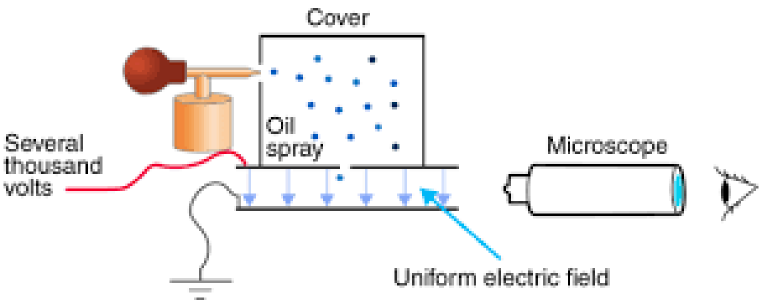


Figure: Mullikan Oil Droplet Method

Atomic Models

Rutherford's Nuclear Model (1911)

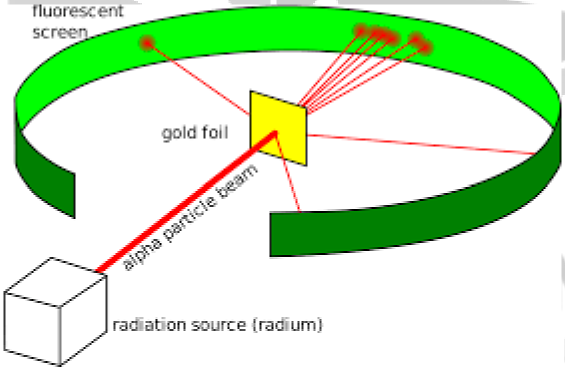
Experiment: Bombarded a thin gold foil with alpha (α) particles.

Observations:

Most α-particles passed through undeflected.

A few were deflected at small angles.

A very small number (1 in 20,000) were deflected backwards.



Conclusions:

The atom is mostly empty space.

It has a small, dense, positively charged core called the **nucleus**, where most of the mass is concentrated.

Electrons revolve around the nucleus.

Defects:

According to classical electromagnetic theory, a revolving electron should continuously lose energy and spiral into the nucleus, causing the atom to collapse. This model could not explain the **stability of the atom**

Planck's Quantum Theory (1900) and Einstein's Photoelectric Effect (1905)

Postulates:

Energy is emitted or absorbed by a body not continuously, but in discrete packets called **quanta** (or **photons** for light).

When an electron jumps from a higher energy level n_2 to a lower level n_1, the energy difference is:

$\Delta E = E_2 - E_1 = 2.18 \times 10^{-18} [1/n_1^2 - 1/n_2^2]$ J/atom

According to Planck's theory, $\Delta E = h\nu = hc/\lambda$.

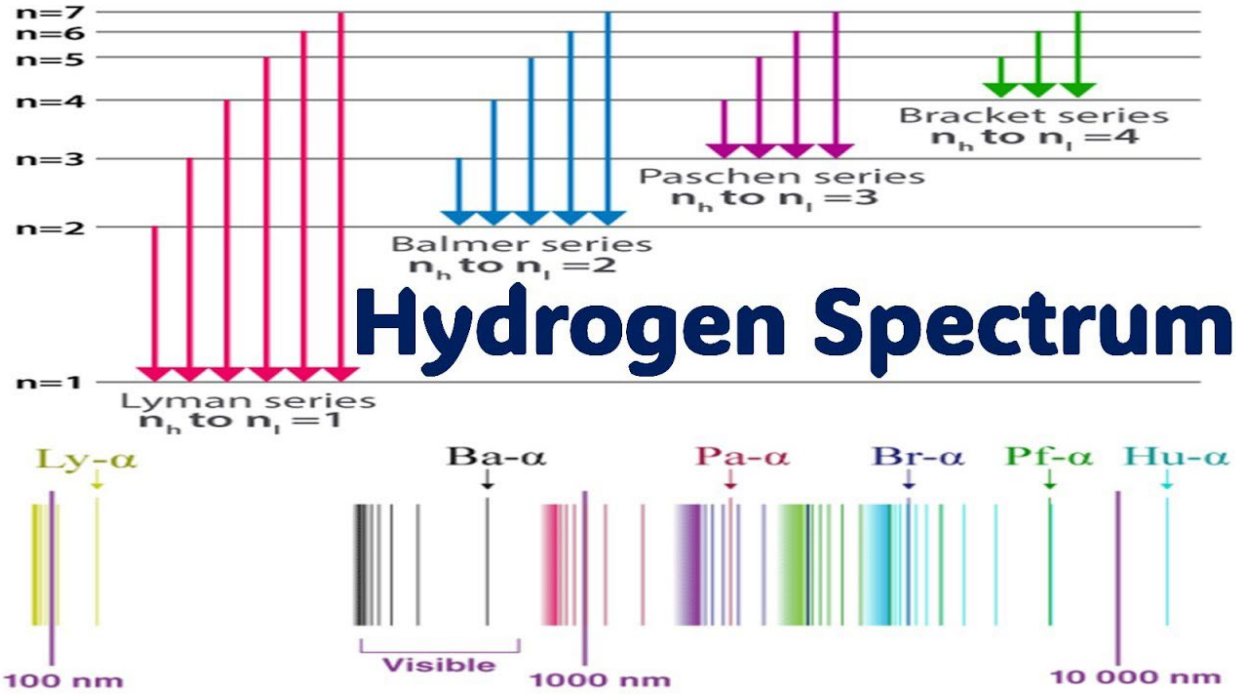
Therefore, the wave number ($\tilde{\nu} = 1/\lambda$) of the emitted photon is:

$\tilde{\nu} = 1/\lambda = R_H [1/n_1^2 - 1/n_2^2]\ m^{-1}$

where R_H is the Rydberg constant ($1.09678 \times 10^7\ m^{-1}$).

Spectral Series of Hydrogen:

Lyman Series: $n_1=1$, $n_2=2, 3, 4...$ (Ultraviolet region)
Balmer Series: $n_1=2$, $n_2=3, 4, 5...$ (Visible region)
Paschen Series: $n_1=3$, $n_2=4, 5, 6...$ (Infrared region)
Brackett Series: $n_1=4$, $n_2=5, 6, 7...$ (Infrared region)
Pfund Series: $n_1=5$, $n_2=6, 7, 8...$ (Infrared region)



Defects of Bohr's Model

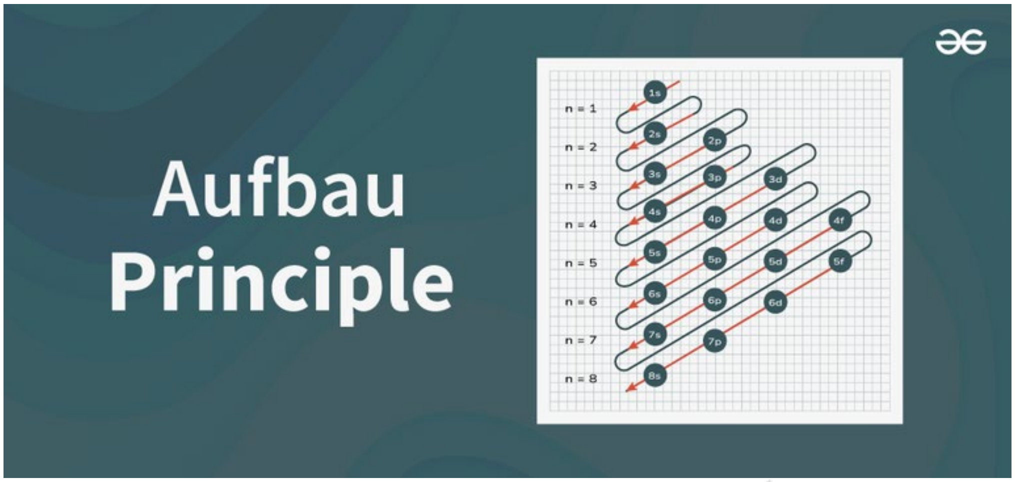
1. It could not explain the spectra of atoms with more than one electron (multi-electron atoms).
2. It failed to explain the **fine structure** of spectral lines (splitting of lines under high resolution).
3. It could not explain the **Zeeman effect** (splitting of spectral lines in a magnetic field) and the **Stark effect** (splitting in an electric field).
4. It violated Heisenberg's Uncertainty Principle by defining precise orbits for electrons.

Quantum Mechanical Model of the Atom

Wave-Particle Duality

De Broglie's Hypothesis (1924): Louis de Broglie proposed that all moving particles have a dual character: they exhibit both particle and wave nature.

Order of filling: 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p



Pauli's Exclusion Principle

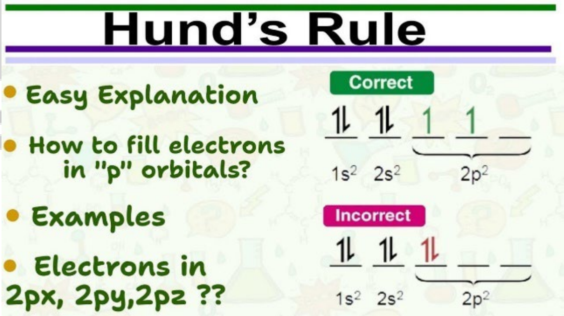
No two electrons in an atom can have the same set of all four quantum numbers.

Consequence: An orbital can hold a maximum of **two electrons**, and they must have opposite spins.

Hund's Rule of Maximum Multiplicity

Electron pairing in degenerate orbitals (orbitals of the same energy, like p_x, p_y, p_z) starts only after each orbital in the subshell is singly occupied. All unpaired electrons in a subshell will have parallel spins.

Example: For a p^3 configuration, the electrons will occupy all three p-orbitals singly with parallel spins, rather than pairing up in fewer orbitals.


Hund's Rule

- Easy Explanation
- How to fill electrons in "p" orbitals?
- Examples
- Electrons in 2px, 2py,2pz ??

X-Rays and Atomic Number

Production and Properties of X-Rays

Discovery: W.C. Roentgen (1895).

Production: Produced when high-energy electrons (cathode rays) strike a heavy metal target (anode) in an X-ray tube.

Properties:

Electromagnetic radiation with very short wavelengths (0.1 Å - 100 Å).

Travel in straight lines.

Not deflected by electric or magnetic fields.

Topic-wise One-Liners on Atomic Structure

Historical Development & Subatomic Particles

1. **Democritus** named the fundamental, indivisible particle of matter **"atomos"**.
2. **John Dalton** established the first scientific atomic theory based on experimental evidence.
3. **J.J. Thomson** discovered the **electron** through his cathode ray tube experiment.
4. The **charge-to-mass ratio (e/m)** of electrons is constant, proving they are a universal constituent of all atoms.
5. **R.A. Millikan**, via his oil-drop experiment, determined the **charge of a single electron**.
6. **E. Goldstein** discovered the **proton** by observing positive rays or canal rays.
7. The **e/m ratio for positive rays** depends on the nature of the gas in the discharge tube.
8. **James Chadwick** discovered the **neutron** by bombarding beryllium with alpha particles.
9. A **proton** is approximately **1836 times heavier** than an electron.
10. The absolute charge of an electron is **-1.602×10^{-19} Coulomb**.

2. Atomic Models

11. **J.J. Thomson's "Plum Pudding Model"** described the atom as a sphere of positive charge with electrons embedded in it.
12. **Rutherford's alpha-particle scattering experiment** led to the proposal of the **nuclear model** of the atom.
13. Rutherford's model concluded that the atom is mostly **empty space** with a small, dense, positively charged **nucleus**.
14. A major defect of Rutherford's model was its inability to explain the **stability of the atom**.
15. **Niels Bohr** combined Rutherford's model with **Planck's quantum theory** to explain the hydrogen spectrum.
16. Bohr's first postulate states that electrons revolve in certain **stationary orbits** without radiating energy.
17. Bohr's model introduced the **quantization of angular momentum**: **$mvr=nh/2\pi$**
18. The radius of the nth orbit in a hydrogen atom is given by **$r=0.529\ n^2 / z$**
19. The energy of an electron in the nth orbit is given by **$E_n=-13.6\ Z^2/n^2$ eV/atom.**
20. The total energy of an electron in a Bohr orbit is **negative**, indicating it is bound to the nucleus.
21. Bohr's model successfully derived the **Rydberg formula** for the hydrogen spectrum.
22. Bohr's model could not explain the **Zeeman effect** (splitting of spectral lines in a magnetic field).
23. Bohr's model violated the **Heisenberg Uncertainty Principle**.

3. Quantum Theory & Spectra

24. **Max Planck** proposed that energy is emitted or absorbed in discrete packets called **quanta**.
25. The energy of a quantum is given by $E=h\nu$, where h is **Planck's constant**.
26. **Albert Einstein** explained the **photoelectric effect** by proposing that light consists of particles called **photons**.
27. In the photoelectric effect, electrons are ejected only if the incident light's frequency is above a certain **threshold frequency**.
28. The hydrogen spectrum consists of several series, including **Lyman (UV)**, **Balmer (Visible)**, and **Paschen (IR)**.
29. The **Rydberg constant** for wavenumber is approximately **109,677 cm^{-1}**.

Practice MCQs

1. According to Bohr's model, the specific permitted circular orbits are referred to as:
A) elliptical paths
B) stationary energy levels
C) quantum jumps
D) magnetic fields
Answer: stationary energy levels

2. The correct relationship between wavelength, frequency, and speed of an electromagnetic wave is:
A) $c = \nu + \lambda$
B) $c = \nu\lambda$
C) $\nu = c\lambda$
D) $\lambda = c/\nu^2$
Answer: $c = \nu\lambda$

3. In the Balmer equation $1/\lambda = R(1/2^2 - 1/n^2)$, the constant R is known as:
A) Planck's constant
B) Rydberg constant
C) Avogadro's number
D) Bohr radius
Answer: Rydberg constant

4. According to the quantum theory of radiation, energy is emitted or absorbed in discrete units called:
A) waves
B) quanta or photons
C) frequencies
D) orbitals
Answer: quanta or photons

5. The kinetic energy of photoelectrons is given by the equation:
A) $1/2mv^2 = h\nu + h\nu_0$
B) $1/2mv^2 = h\nu_0 - h\nu$
C) $1/2mv^2 = h\nu - h\nu_0$
D) $1/2mv^2 = h\nu_0$
Answer: $1/2mv^2 = h\nu - h\nu_0$

6. The Compton effect demonstrated that X-rays exhibit particle-like behavior because they can:
A) be diffracted
B) be refracted
C) knock out electrons from a surface
D) produce continuous spectra
Answer: knock out electrons from a surface

7. The radius of the nth orbit in the hydrogen atom according to Bohr's model is given by:
A) $r = n \times 0.529 \times 10^{-8}$ cm
B) $r = n^2 \times 0.529 \times 10^{-8}$ cm
C) $r = 0.529 \times 10^{-8}$ cm
D) $r = 0.529 \times 10^{-10}$ cm
Answer: $r = n^2 \times 0.529 \times 10^{-8}$ cm

8. The energy of an electron in the nth orbit of a hydrogen atom is:
A) directly proportional to n^2
B) directly proportional to n
C) inversely proportional to n^2
D) inversely proportional to n
Answer: inversely proportional to n^2

9. The spectral series of hydrogen that lies in the infrared region is the:
A) Lyman series
B) Balmer series
C) Paschen series
D) Pfund series
Answer: Paschen series

10. A significant shortcoming of the Bohr model was its inability to explain:
A) the hydrogen spectrum
B) the stability of the hydrogen atom
C) the spectra of atoms with more than one electron
D) the quantization of angular momentum
Answer: the spectra of atoms with more than one electron

11. According to Sommerfeld's modification of the Bohr model, electron orbits could be:
A) only circular
B) only elliptical
C) both circular and elliptical
D) parabolic
Answer: both circular and elliptical

12. The maximum number of electrons that can be accommodated in an orbit designated by principal quantum number n is:
A) 2n
B) n^2
C) $2n^2$

The Gaseous State

Introduction to States of Matter

Matter exists primarily in four states: **Solid, Liquid, Gas, and Plasma**.

Solids: Have a definite shape and volume. Particles are tightly packed in a fixed, orderly arrangement and can only vibrate.

Liquids: Have a definite volume but no definite shape; they take the shape of their container. Particles are close together but can move past one another (flow).

Gases: Have no definite shape or volume. They expand spontaneously to fill their container. Particles are far apart, move rapidly and randomly, and have high kinetic energy.

Plasma: A fourth state of matter consisting of an ionized gas with positive ions and free electrons. It is macroscopically neutral and responds strongly to electromagnetic fields

Example of plasma

(Stars, neon signs).

The gaseous state is the simplest to study and model mathematically due to the minimal intermolecular forces and large separations between molecules.

General Properties and Characteristics of Gases

Gases exhibit unique properties due to the large spaces between their molecules and their high kinetic energy.

Expansibility: Gases expand indefinitely to fill the entire volume of their container.

Compressibility: Gases can be easily compressed into a smaller volume by applying pressure due to the large amount of space between molecules (e.g., LPG, CNG).

Diffusibility: Gases mix spontaneously and rapidly with each other to form a homogeneous mixture.

Diffusion: The spontaneous intermingling and mixing of gas molecules (e.g., the smell of perfume spreading in a room).

Effusion: The process by which gas molecules escape from a container through a tiny hole or porous plug into a vacuum or region of lower pressure without collisions.

Exertion of Pressure: Gas molecules constantly collide with the walls of their container, exerting pressure. This pressure is due to the force of these numerous collisions per unit area and is exerted uniformly in all directions.

Low Density: Densities are much lower than those of liquids and solids because molecules are widely spaced.

Parameters (State Variables) of a Gas

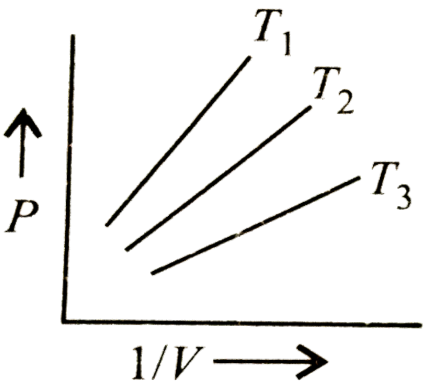
A gas sample is completely described by four measurable properties:

Pressure (P):

The force exerted by gas molecules per unit area of the container wall.

SI Unit: Pascal (Pa).

Common Units: atmosphere (atm), millimeter of mercury (mm Hg), torr, bar.



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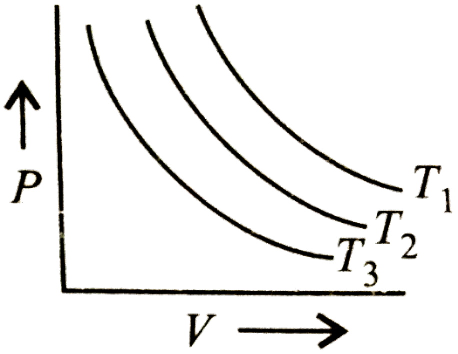

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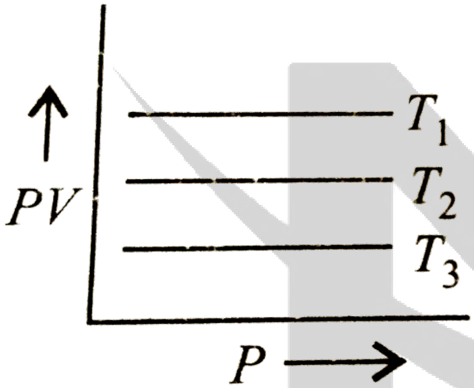

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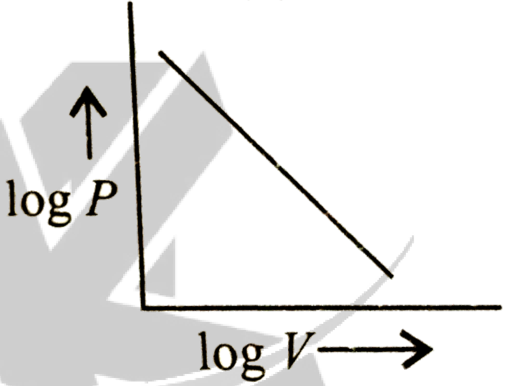


(iv)

Charles's Law (Volume-Temperature Relationship)

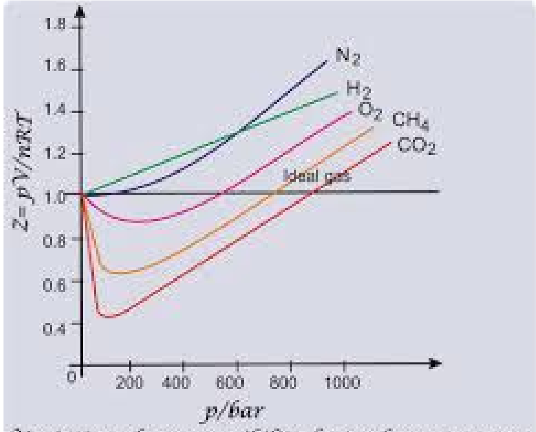
Statement: For a fixed amount of gas at constant pressure, the volume of the gas is directly proportional to its absolute temperature (Kelvin).

Mathematical Expression: $V \propto T$ (constant n, P) or $\mathbf{V/T = k}$ or $\mathbf{V_1/T_1 = V_2/T_2}$

Explanation (KMT): Increasing temperature increases molecular speed. Molecules hit the walls more frequently and with greater force. To keep pressure constant, the volume must increase.

Absolute Zero: This is absolute zero (0 K). Absolute zero is theoretically approached but not attained; extrapolation of ideal gas V–T gives **−273.15 °C.**

- At 0 K (idealized limit**), translational kinetic energy** approaches zero.”



Variation of compressibility factor for some gases

Van der Waals Equation

This equation modifies the ideal gas equation to account for real gas behavior.

For n moles: $[P + a(n^2/V^2)] (V - nb) = nRT$

For 1 mole: $[P + a/V^2] (V - b) = RT$

Significance of Constants:

'a': Corrects for intermolecular attractive forces. Units: atm L^2 mol^{-2}. Larger 'a' means stronger attractions.

'b': Corrects for the finite volume of gas molecules (excluded volume). Units: L mol^{-1}. Larger 'b' means larger molecular size.

Liquefaction of Gases & Critical Phenomena

Gases can be liquefied by applying high pressure and cooling below a specific temperature.

Critical Constants:

Critical Temperature (T_c): The highest temperature at which a gas can be liquefied by pressure alone.

Critical Pressure (P_c): The minimum pressure required to liquefy a gas at its critical temperature.

Critical Volume (V_c): The volume occupied by one mole of the gas at its Tc and Pc.

Relation with van der Waals Constants:

$V_c = 3b$

$P_c = a / 27b^2$

$T_c = 8a / (27Rb)$

Joule-Thomson Effect:

- When a compressed gas is allowed to expand adiabatically through a porous plug or nozzle into a region of lower pressure, it cools down. This cooling is used in gas liquefaction processes like **Linde's Method** for liquefying air.
- At room temperature H_2 and He do not cool on JT expansion (low inversion temperature); pre-cooling below inversion temperature is required.

Topic-Wise One-Liners: The Gaseous State

1. Introduction to States of Matter

1. Matter primarily exists in four states: **Solid, Liquid, Gas, and Plasma**.
2. **Solids** have a definite shape and volume with particles in a fixed, orderly arrangement.
3. **Liquids** have a definite volume but no definite shape, taking the shape of their container.
4. **Gases** have no definite shape or volume, expanding spontaneously to fill their container.
5. **Plasma** is an ionized gas consisting of positive ions and free electrons, found in stars and neon signs.
6. The **gaseous state** is the simplest to study mathematically due to minimal intermolecular forces.

2. General Properties of Gases

7. **Expansibility** is the property of gases to expand indefinitely and fill the entire volume of their container.

8. **Compressibility** allows gases to be easily reduced in volume by applying pressure (e.g., LPG, CNG).

9. **Diffusibility** is the spontaneous and rapid mixing of gases to form a homogeneous mixture.

10. **Diffusion** is the intermingling of gas molecules (e.g., perfume smell spreading in a room).

11. **Effusion** is the escape of gas molecules through a tiny hole into a vacuum without collisions.

12. Gases exert **pressure** due to constant collisions of molecules with the container walls.

13. Gases have **low density** because their molecules are widely spaced.

3. Parameters (State Variables) of a Gas

14. A gas sample is described by four parameters: **Pressure (P), Volume (V), Temperature(T), and Amount (n)**.

15. The **SI unit of pressure** is Pascal (Pa); common units include atm, mm Hg, torr, and bar.

16. **Standard conversions**: 1 atm = 760 mm Hg = 760 torr = 1.013×10^5 Pa = 1.013 bar.

17. Pressure is measured by a **manometer** for gas samples and a **barometer** for atmospheric pressure.

18. The **SI unit of volume** is cubic metre (m^3); common units are litre (L) and millilitre (mL).

19. The **SI unit of temperature** for gas laws is **Kelvin (K)**, where K = °C + 273.15.

20. The **amount of gas (n)** is expressed in moles, calculated as n = mass (m) / Molar mass (M).

4. The Gas Laws

21. **Boyle's Law**: For a fixed mass of gas at constant temperature, volume is inversely proportional to pressure ($V \propto 1/P$ or $P_1V_1 = P_2V_2$).

22. A plot of **P vs. V** at constant temperature is a hyperbola called an **isotherm**.

23. **Charles's Law**: For a fixed mass of gas at constant pressure, volume is directly proportional to its absolute temperature ($V \propto T$ or $V_1/T_1 = V_2/T_2$).

24. **Absolute Zero (0 K or -273.15 °C)** is the temperature where the volume of an ideal gas becomes zero.

Practice MCQs

1. According to Boyle's law, for a fixed amount of gas at constant temperature, the volume is:

A) directly proportional to its pressure
B) inversely proportional to its pressure
C) directly proportional to the square of its pressure
D) independent of its pressure

Answer: inversely proportional to its pressure

2. Mathematically, Charles's law can be represented as:

A) $V \propto P$
B) $V \propto 1/T$
C) $V \propto T$
D) $P \propto T$

Answer: $V \propto T$

3. The value of the universal gas constant R in litre-atm K^{-1} mol^{-1} is:

A) 8.314
B) 0.0821
C) 1.987
D) 62.364

Answer: 0.0821

4. At Standard Temperature and Pressure (STP), one mole of any ideal gas occupies a volume of:

A) 20.0 L
B) 22.4 L
C) 24.8 L
D) 25.0 L

Answer: 22.4 L

5. Dalton's law of partial pressures states that the total pressure of a mixture of non-reacting gases is equal to the:

A) average of the partial pressures
B) product of the partial pressures
C) sum of the partial pressures
D) difference of the partial pressures

Answer: sum of the partial pressures

6. Graham's law of diffusion states that the rate of diffusion of a gas is inversely proportional to the:

A) square of its density
B) square root of its molar mass
C) square of its molar mass
D) square root of its density

Answer: square root of its molar mass

7. According to the kinetic molecular theory, the average kinetic energy of gas molecules is directly proportional to the:

A) square of the absolute temperature
B) square root of the absolute temperature
C) absolute temperature
D) pressure of the gas

Answer: absolute temperature

8. The root mean square velocity (u) of a gas molecule is given by:

A) $\sqrt{(2RT/M)}$
B) $\sqrt{(3RT/M)}$
C) $\sqrt{(8RT/\pi M)}$
D) $\sqrt{(RT/M)}$

Answer: $\sqrt{(3RT/M)}$

9. The compressibility factor (Z) for an ideal gas is always:

A) 0
B) 1
C) less than 1
D) greater than 1

Answer: 1

10. The van der Waals constant 'a' accounts for:

A) the finite volume of gas molecules
B) the universal gas constant
C) intermolecular attractive forces
D) the temperature of the gas

Answer: intermolecular attractive forces

11. The critical temperature of a gas is defined as the temperature:

A) at which it solidifies

States of Matter - Liquids and Solids

Kinetic Molecular Theory of Liquids and Solids

Postulates for Liquids

Composition and Proximity: A liquid consists of atoms, ions, or molecules that are in close contact with one another, resulting in negligible empty space between them.

Motion: The particles are in constant, random motion. However, this motion is restricted by the close packing; they cannot move freely but can slide past one another, which is why liquids can flow.

Intermolecular Forces: The attractive forces between liquid molecules are stronger than those in gases but significantly weaker than those in solids. These forces are insufficient to hold the particles in fixed positions.

Kinetic Energy: The average kinetic energy of the liquid molecules is directly proportional to the absolute temperature. At a given temperature, the average kinetic energy of the liquid molecules is equal to that of its vapor molecules.

Postulates for Solids

Composition and Packing: Solids are composed of atoms, ions, or molecules that are closely packed together in a fixed, orderly arrangement.

Intermolecular Forces: The particles are held together by very strong intermolecular (or ionic/covalent/metallic) forces of attraction.

Rigidity and Motion: Solids are rigid and possess a definite shape because their particles are locked in place and cannot translate or rotate. They can only vibrate about their mean positions.

Order and Arrangement: The particles in solids exhibit a high degree of long-range order, arranged in regular, three-dimensional patterns called a crystal lattice (for crystalline solids).

Compressibility and Density: There is very little empty space between particles, making solids virtually incompressible. This close packing results in high density.

Intermolecular Forces

Intermolecular forces are the attractive forces *between* molecules. They are much weaker than intramolecular forces (covalent, ionic bonds) that hold atoms together *within* a molecule. Collectively, these weak forces are known as **Van der Waals forces** Van der Waals forces (in the standard/IUPAC sense) include dipole–dipole, dipole-induced dipole, and London dispersion forces,hydrogen bonding is usually discussed separately as a special, stronger, directional interaction..

Types of Intermolecular Forces

A. Dipole-Dipole Forces

Definition: These are the attractive forces between the positive end (δ+) of one polar molecule and the negative end (δ-) of another polar molecule.

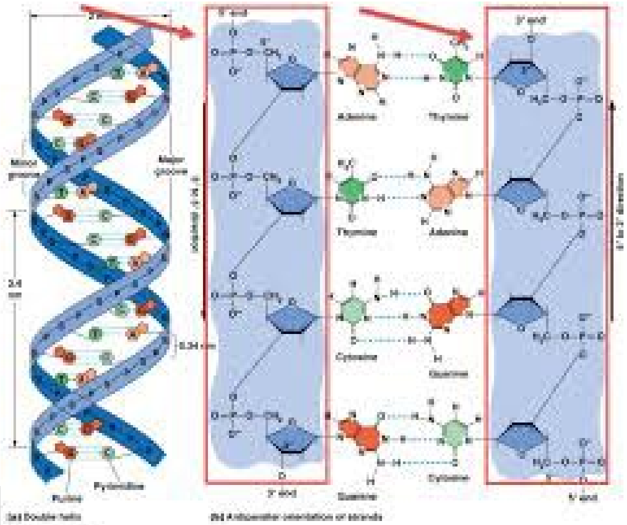
Explanation: In polar molecules (e.g., HCl, HBr, $CHCl_3$), a permanent dipole exists due to the difference in electronegativity between bonded atoms. These molecular dipoles align so that opposite charges attract.

Strength: They are approximately 1% as strong as a covalent bond (0.5 - 2 kcal/mol) and are effective only at short distances.

Effect on Properties: Stronger dipole-dipole forces lead to higher melting points, boiling points, and heats of vaporisation.

B. Hydrogen Bonding

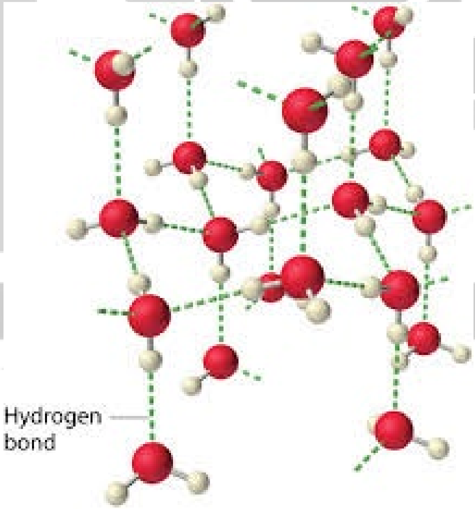
DNA: The double-helix structure is held together by hydrogen bonds between complementary nitrogenous bases (A-T, G-C).



- **Structure of Ice:** In ice, water molecules form an open, tetrahedral, cage-like structure due to extensive hydrogen bonding, creating empty spaces. This makes ice less dense than liquid water, causing it to float.

Other Applications: Cleaning action of soaps and detergents (by reducing surface tension), adhesive action of paints and dyes, and the viscous, sticky nature of substances like glue and honey.

Structure of ice



Physical Properties of Liquids

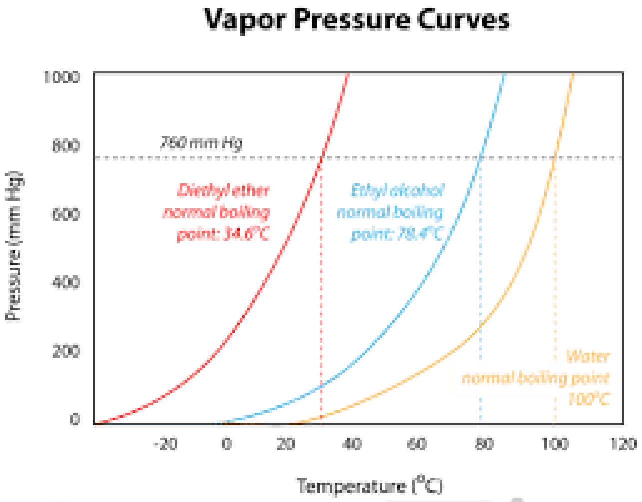
Evaporation

Definition: The spontaneous change of a liquid into its vapour at the surface of the liquid, occurring at any temperature below the boiling point.

Kinetic Molecular Explanation: Molecules in a liquid have a distribution of kinetic energies. The high-energy molecules near the surface can overcome intermolecular forces and escape into the vapour phase.

Cooling Effect: Evaporation causes cooling because when the most energetic molecules leave, the average kinetic energy (and thus temperature) of the remaining liquid decreases.

Manometer instrumentation



[Graph: Vapor Pressure vs. Temperature]

Boiling Point

Definition: The temperature at which the vapour pressure of a liquid becomes equal to the external (atmospheric) pressure. At this point, bubbles of vapour form throughout the liquid.

Explanation: The kinetic energy of the molecules becomes sufficient to overcome intermolecular forces throughout the bulk liquid, causing it to vaporize. The temperature remains constant until all liquid has vaporized.

Molar Heat of Vaporization (ΔH_{vap}): The amount of heat required to vaporize one mole of a liquid at its boiling point. For water, $\Delta H_{vap} = 40.7$ kJ/mol.

Dependence on Pressure:

Lower External Pressure = Lower Boiling Point. (e.g., water boils below 100°C on high mountains).

Higher External Pressure = Higher Boiling Point. (e.g., in a pressure cooker, water boils above 100°C, cooking food faster).

Normal Boiling Point: The boiling point at a standard pressure of 1 atm (760 torr).

Vacuum Distillation: A technique where distillation is carried out under reduced pressure to lower the boiling point and prevent decomposition of heat-sensitive liquids (e.g., purification of glycerin).

Viscosity

Definition: Viscosity (η) is a measure of a liquid's internal resistance to flow. It arises from internal friction between layers of molecules as they slide past one another.

Explanation: When a liquid flows, layers near the container walls move slower than layers in the center. This velocity gradient (dv/dx) leads to frictional resistance. According to Newton's law, $F = \eta A\,(dv/dx)$, where η is the coefficient of viscosity.

Units: The SI unit is Pascal-second (Pa.s) or kg m^{-1} s^{-1}. The CGS unit is Poise (P), where 1 Pa.s = 10 P. Fluidity (φ) is the reciprocal of viscosity ($\varphi = 1/\eta$).

Factors Affecting Viscosity:

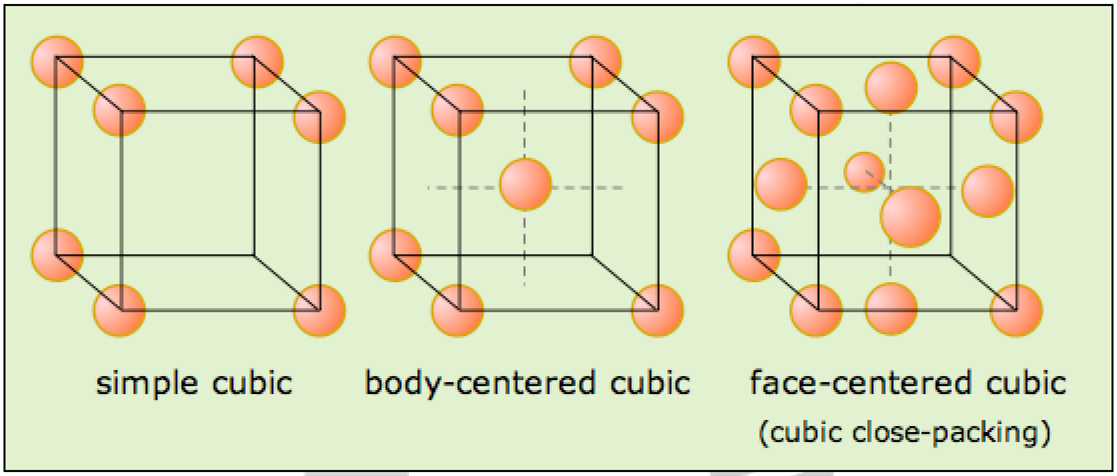
Intermolecular Forces: Stronger forces lead to higher viscosity (e.g., honey has high viscosity due to hydrogen bonding and large molecular size).

Molecular Size and Shape: Large, irregular molecules that can tangle have higher viscosities.

Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Sugar, Monoclinic Sulphur, Gypsum
Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$K_2Cr_2O_7$, $CuSO_4\cdot 5H_2O$
Hexagonal	a = b ≠ c	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, Ice
Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite ($CaCO_3$), $NaNO_3$, Cinnabar

Cubic Unit Cells

1. **Simple Cubic (SC):** Lattice points only at the corners. Atoms/unit cell = 1. Coordination Number = 6.
2. **Body-Centered Cubic (BCC):** One lattice point at the center of the cube. Atoms/unit cell = 2. Coordination Number = 8. (e.g., Fe, Na, W).
3. **Face-Centered Cubic (FCC):** One lattice point at the center of each face. Atoms/unit cell = 4. Coordination Number = 12. (e.g., Cu, Ag, Au, Al, NaCl).



**(Three cubes side-by-side. SC: Spheres only at corners.
BCC: Spheres at corners and one in the center.
FCC: Spheres at corners and one in the center of each face.)**

Calculation of Density of a Crystal

The density (ρ) can be calculated from unit cell properties:

ρ = (Mass of unit cell) / (Volume of unit cell) = (Z × M) / (N_A × a^3)

Where: Z = number of atoms per unit cell, M = molar mass (g/mol), N_A = Avogadro's number, a = edge length of the unit cell (cm).

X-Ray Crystallography and Bragg's Law

Principle: X-rays have wavelengths comparable to interatomic distances, so crystals act as diffraction gratings.

Bragg's Law: The condition for constructive interference is given by: **$n\lambda = 2d \sin\theta$**
Where: n = order of reflection, λ = wavelength of X-rays, d = interplanar spacing, θ = glancing angle.

$Na^{+}(g) + Cl^{-}(g) \rightarrow \text{NaCl}(s)$

Lattice energy:

-787 kJ/mol

This value indicates that when gaseous sodium ions and gaseous chloride ions come together to form a mole of solid sodium chloride, 787 kJ of energy is released.

Factors Affecting Lattice Energy:

Ionic Charge: Higher charges lead to stronger attraction and higher lattice energy (e.g., MgO > NaCl).

Ionic Size: Smaller ions can get closer, leading to stronger attraction and higher lattice energy.

Significance: Higher lattice energy indicates stronger ionic bonding, resulting in higher melting points, lower solubility, and greater crystal stability.

Topic-Wise One-Liners: Solid & Liquid State

PART 1: SOLID STATE

1. Types of Solids

1. **Solids** have a definite volume and shape and are rigid due to the inability of their particles to translate.
2. **Crystalline solids** have a regular, repeating three-dimensional arrangement of particles called a crystal lattice.
3. Examples of crystalline solids are sugar, salt, diamond, and most metals.
4. **Amorphous solids** have a random, disordered arrangement of particles and lack a well-defined crystal lattice.
5. Examples of amorphous solids are glass, rubber, and plastics.
6. Amorphous solids are considered **super-cooled liquids** due to their disordered structure, evident in the flow of old glass panes.

2. Isotropy and Anisotropy

7. **Isotropy** is the property of having identical values of physical properties in all directions, characteristic of amorphous solids.

8. **Anisotropy** is the property where the magnitude of a physical property varies with direction, characteristic of crystalline solids.

9. Anisotropy in crystals arises from the different arrangement of particles in different directions.

3. Crystal Habit and Symmetry

10. The external shape of a crystal is called its **habit**.

11. The plane surfaces of a crystal are called **faces**, and the angles between them are **interfacial angles**.

12. The constancy of interfacial angles is a fundamental characteristic of a given crystalline substance.

13. A **plane of symmetry** divides a crystal into two halves that are mirror images of each other.

14. An **axis of symmetry** is an imaginary line about which rotating the crystal brings it into an equivalent position more than once in a 360° rotation.

15. A **centre of symmetry** is a point in the crystal such that any line drawn through it meets the surface at equal distances on opposite sides.

4. Crystal Lattice and Unit Cell

16. A **crystal lattice** is a regular, three-dimensional arrangement of points representing the positions of particles in the crystal.

17. The smallest repeating unit of a crystal lattice that generates the entire crystal is called a **unit cell**.

18. A **primitive unit cell** has lattice points only at its corners.

Practice MCQs – States of Matter (Liquids and Solids)

1. The intermolecular forces present between molecules in liquids and solids are collectively called
A) ionic bonds
B) van der Waals forces
C) coordinate bonds
D) metallic bonds
Answer: van der Waals forces

2. Which intermolecular force arises between permanent dipoles of polar molecules?
A) London dispersion force
B) dipole-dipole force
C) ion-dipole force
D) covalent bonding
Answer: dipole-dipole force

3. Hydrogen bonding is most commonly observed when hydrogen is covalently bonded to
A) Cl, Br, or I
B) F, O, or N
C) S, P, or Cl
D) C, Si, or Ge
Answer: F, O, or N

4. London dispersion forces are especially important in
A) highly ionic compounds
B) non-polar molecules
C) network covalent solids
D) aqueous electrolyte solutions
Answer: non-polar molecules

5. The partial positive end of one HCl molecule attracts the partial negative end of another HCl molecule due to
A) ion-dipole attraction
B) dipole-dipole attraction
C) metallic bonding
D) hydrogen bonding
Answer: dipole-dipole attraction

6. Dipole-induced dipole forces arise when
A) two ions attract each other
B) a polar molecule induces polarity in a non-polar molecule
C) a hydrogen atom bonds to fluorine
D) atoms share electrons equally
Answer: a polar molecule induces polarity in a non-polar molecule

7. The weak attraction between an instantaneous dipole and an induced dipole is called
A) hydrogen bonding
B) London force
C) ionic bonding
D) covalent bonding
Answer: London force

8. According to the text, London dispersion forces become stronger when
A) molecular size decreases
B) electronic cloud becomes more easily distorted
C) molecules become less polarizable
D) temperature becomes zero only
Answer: electronic cloud becomes more easily distorted

9. Polarizability is the measure of
A) the ionic radius of an atom
B) the extent to which the electronic cloud can be distorted
C) the number of covalent bonds in a molecule
D) the mass of the nucleus
Answer: the extent to which the electronic cloud can be distorted

10. The boiling points of noble gases increase from helium to radon mainly because
A) their ionic character increases
B) their polarizability increases
C) their hydrogen bonding increases
D) their covalent bond strength decreases
Answer: their polarizability increases

11. Among halogens, iodine exists as a solid at room temperature mainly due to
A) strong ionic bonding
B) high polarizability and stronger London forces
C) hydrogen bonding
D) metallic bonding
Answer: high polarizability and stronger London forces

12. The higher boiling point of n-pentane than neopentane is due to

Chemical Bonding and Molecular Structure

Introduction to Chemical Bonds

Definition:

A **chemical bond** *is defined as the attractive force that holds two or more atoms together in a stable molecule or ion.*

This force results from the electrostatic interactions between the electrons and nuclei of the combining atoms. A **chemical bond** represents the fundamental force responsible for the cohesion of atoms and ions, leading to the formation of the vast array of chemical compounds known to science. This force of attraction, which operates between the constituent particles, is the direct consequence of chemical combination. The overarching goal of chemical bonding theory is to elucidate the mechanisms by which these bonds form, the forces that govern their stability, and the three-dimensional architectures of the resulting molecules.

Why bonds Formation Occur?

A particularly illuminating case is that of the noble gases: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). These elements exhibit a profound chemical inertness under standard conditions. Their electronic configurations are characterized by completely filled valence shells: helium possesses the stable duplet configuration **$1s^2$**, while the others conform to the general pattern **ns2*np*6,** signifying a complete octet of electrons in their outermost principal quantum level. This electronic arrangement confers exceptional stability, rendering these gases largely unreactive. Indeed, a noble gas does not react with another noble gas.

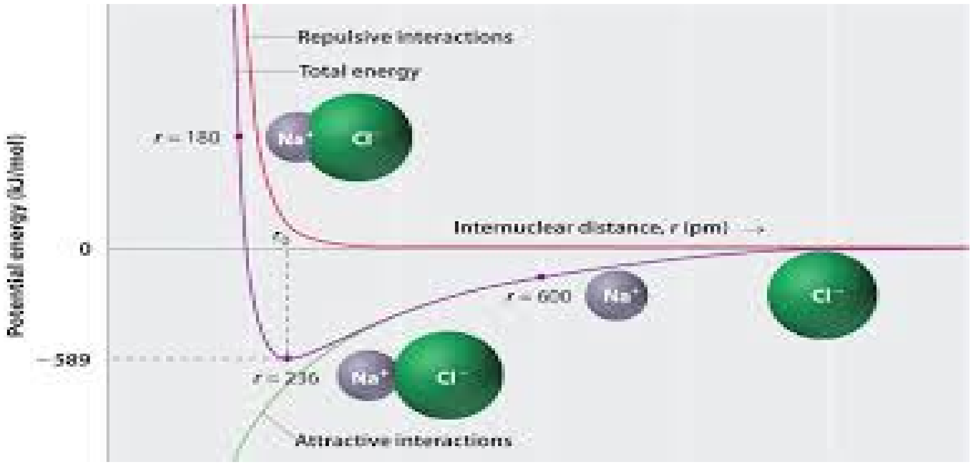
ENERGETICS OF BOND FORMATION

A very fine example of Energy involved during bond **formation is H_2**.When two isolated hydrogen atoms, each with its single 1s electron, are infinitely separated, the potential energy of the system is arbitrarily set to zero. As these atoms begin to approach each other under the influence of mutual attraction, several forces come into play simultaneously. **Attractive forces** arise between the nucleus of one atom and the electron of the other, and vice-versa. These forces tend to pull the atoms closer together. Concurrently, **repulsive forces** emerge: repulsion between the two positively charged nuclei and repulsion between the two negatively charged electrons. These forces tend to push the atoms apart.

The net potential energy of the two-atom system is the balance of these attractive and repulsive interactions. Initially, as the internuclear distance decreases from infinity, the magnitude of the attractive forces increases more rapidly than that of the repulsive forces. Consequently, the net force is attractive, and the **potential energy of the system decreases** as the atoms approach.

For the hydrogen molecule, this minimum occurs at an internuclear distance of **74 picometers (pm)**. This specific distance is known as the **bond length**, **bond distance**, or **equilibrium bond distance**. It represents a "**compromise distance**" where the attractive and repulsive forces are balanced, resulting in the lowest possible potential energy for the H_2 molecule.

The depth of this potential energy well, measured from the zero-energy reference of separated atoms, quantifies the strength of the bond. For H_2, the energy released when one mole of H_2 molecules is formed from its constituent atoms is **436.45 kilojoules per mole (kJ mol^{-1})**. This quantity is termed the **bond formation energy** or, more commonly, the **bond dissociation energy (D)**.



Fundamental Goal of Bond Formation:

Atoms form chemical bonds to achieve a lower energy state, thereby increasing their stability compared to their isolated forms. A stable chemical bond is formed only when the total energy of the system decreases as the atoms approach each other. The **Octet Rule** posits that during chemical bond formation, atoms tend to gain, lose, or share electrons in such a manner that each atom attains a maximum of eight electrons in its valence shell, mirroring the electronic configuration of noble gases (except helium). This rule provides a powerful, albeit simplified, framework for predicting the stoichiometry of a vast number of compounds.

Consider the following illustrative examples:

- **Lithium (Li):** Configuration **$1s^{2},2s^{1}$**. By losing its single valence electron, it forms the Li+ ion, achieving the stable helium configuration 1s2
- **Magnesium (Mg):** Configuration **$1s^{2},2s^{2},2p^{6}3s^{2}$** Loss of two electrons yields Mg^{2}+, attaining the neon configuration **$1s^{2},2s^{2},2p^{6}$.**
- **Fluorine (F):** Configuration **$1s^{2},2s^{2},2p^{5}$**. Gaining one electron forms the F^{-} ion, achieving the neon octet.

The driving force for bond formation is thus the attainment of a more stable, lower-energy electronic configuration. However, the pathway to this stability—whether by complete electron transfer or by mutual sharing—depends on the specific properties of the interacting atoms, such as their ionization energies, electron affinities, and electronegativity. In some reactions, an atom may exhibit an *apparent* ambiguity in its tendency.

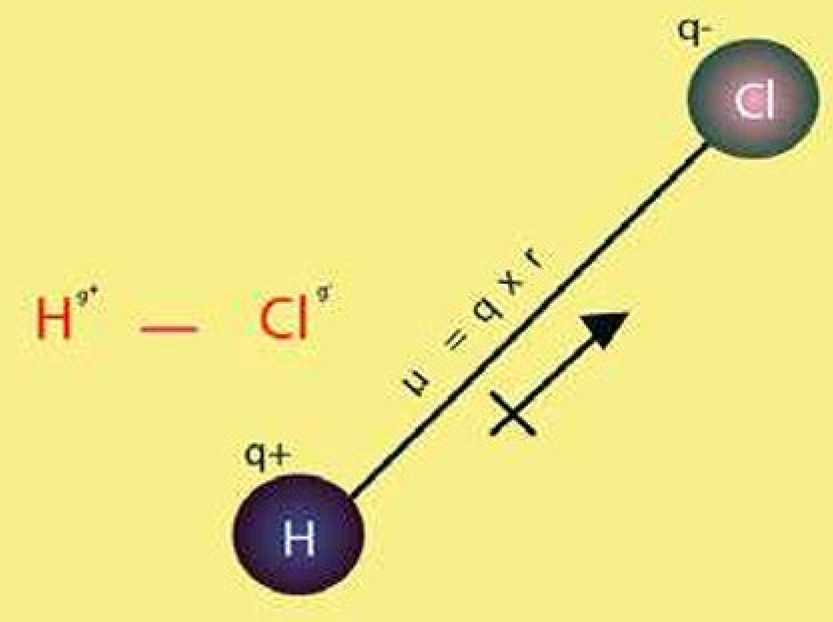
For instance, in the formation of sodium hydride **(NaH),** hydrogen acts as an electron acceptor, forming H−. Conversely, in hydrogen fluoride (HF), the hydrogen atom, while still bonded, donates the major share of its electron density to the highly electronegative fluorine. These behaviors are not contradictions but rather reflections of the relative energies involved in different chemical contexts.

Limitations and Exceptions to the Octet Rule:

Incomplete Octet: Some molecules have less than 8 electrons around the central atom (e.g., $BeCl_2$ has 4, BF_3 has 6).

Odd-Electron Molecules (Free Radicals): Molecules with an odd number of valence electrons cannot pair all electrons (e.g., NO, NO_2).

Expanded Octet (Super-Octet): Central atoms from the 3rd period and beyond can accommodate more than 8 electrons by utilizing empty d-orbitals **(e.g., PCl_5 with 10 electrons, SF_6 with 12 electrons).**



where ris the displacement vector pointing from the negative to the positive charge. In chemistry, for a bond $A\delta^+$—$B\delta^-$, it points from δ^+ to δ^-.

Units: The SI unit is the **coulomb-meter (C m).** The more common unit is the **Debye (D)**, where $1D = 3.336 \times 10{-}30$ C m.

For a Diatomic Molecule: The dipole moment is the **bond dipole moment**. Examples: HF (1.91 D), HCl (1.08 D), HBr (0.82 D), HI (0.44 D). The decrease reflects decreasing polarity.

For Polyatomic Molecules: The molecular dipole moment is the **vector sum** of all individual bond dipole moments (and lone pair moments). It depends on both bond polarity and molecular geometry.

Symmetrical Molecules: If the geometry is such that the bond dipoles cancel each other, the molecule is **nonpolar** ($\mu = 0$).

CO_2 (linear): Two equal C=O dipoles point in opposite directions → cancel. $\mu = 0$.

BF_3 (trigonal planar): Three B-F dipoles cancel at 120° → $\mu = 0$.

CCl_4, CH_4(tetrahedral): Four bond dipoles cancel → $\mu = 0$.

SF6 (octahedral): $\mu = 0$.

Asymmetrical Molecules: If the bond dipoles do not cancel, the molecule has a net dipole moment (**polar molecule**).

H_2O (bent): Two O-H dipoles do not cancel → $\mu = 1.85$ D.

NH_3 (trigonal pyramidal): Three N-H dipoles do not cancel → $\mu = 1.47$ D.

CH_3Cl (tetrahedral but not symmetric due to different substituents): The C-Cl dipole is not cancelled by the three C-H dipoles → $\mu = 1.87$ D.

SO_2 (bent): $\mu = 1.63$ D.

Applications of Dipole Moment

1. **Determining Percentage Ionic Character:**

$$\%\text{Ionic Character} = \mu_{\textbf{observed}} / \mu_{\textbf{ionic}} \times 100$$

Where *i*onicis the dipole moment calculated assuming complete electron transfer (**$q = 1.602 \times 10{-}19$ C)** and the experimental **bond length (r).**

Example for HF:

%Ionic Character=(1.91/4.40)×100=43.4%

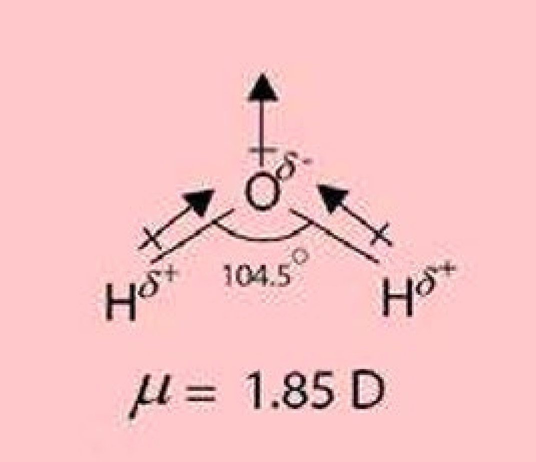
Where 1.91 is observed dipole moment

And 4.40 is ionic dipole moment

2. **Determining Molecular Geometry:**
3. The measured dipole moment can distinguish between possible geometries.

CO_2has $\mu = 0$, confirming a **linear** structure (a bent structure would have $\mu > 0$).

H_2O has $\mu = 1.85$ D, confirming a **bent** structure (a linear structure would have $\mu = 0$).



BF_3 has $\mu = 0$, confirming a **trigonal planar** structure (a pyramidal shape would have $\mu > 0$).

For H_2S and SO_2, which are polar molecules, dipole moment is not zero**.**

Valence Shell Electron Pair Repulsion (VSEPR) Theory

Basic Principle:

The VSEPR theory states that **electron pairs (both bonding and lone pairs) in the valence shell of a central atom repel each other** and arrange themselves in space to be as far apart as possible. This arrangement of electron pairs determines the electron-pair geometry, while the positions of the atoms define the molecular geometry.

Order of Repulsion:

Lone pair-Lone pair (lp-lp) > Lone pair-Bond pair (lp-bp) > Bond pair-Bond pair (bp-bp)

Steps to Predict Molecular Shape:

1. Draw the Lewis structure of the molecule/ion.
2. Count the total number of electron pairs around the central atom (bonding pairs + lone pairs).

Pi (π) Bond:

Formed by the **sidewise (lateral) overlap** of p-orbitals perpendicular to the internuclear axis.

Characteristics:

Stability $\propto \frac{1}{\pi\ bond}$

Reactivity $\propto$ No. of π bond

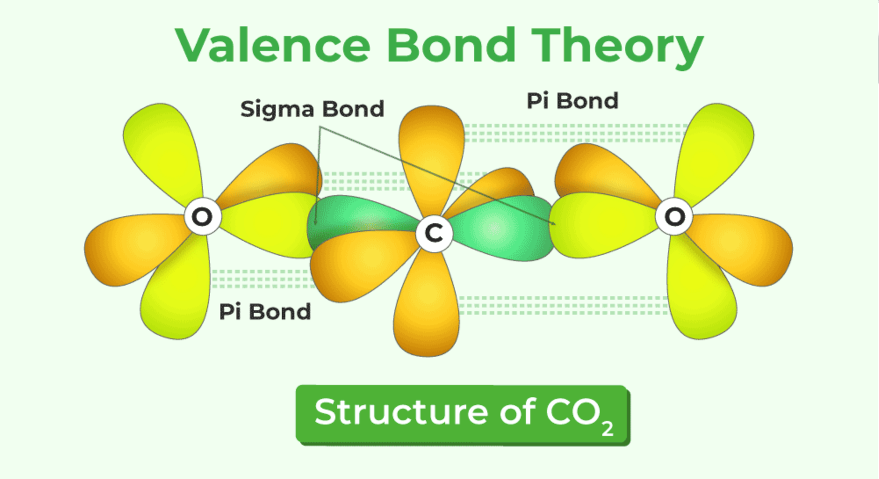
Does not affect the geometry of molecule

Pi bond shortens the bond length

Higher bond order (including pi bonds) results in shorter bond length

Differences between Sigma (σ) and Pi (π) Bonds:

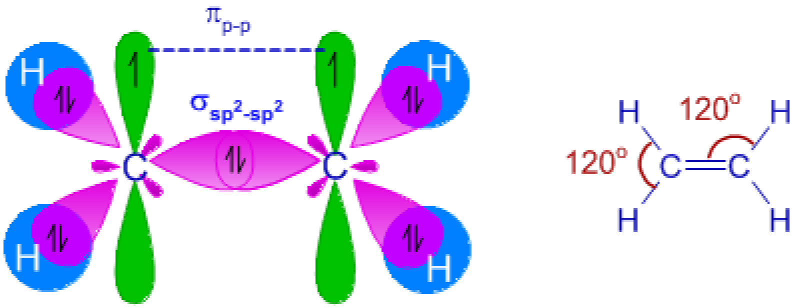
Property	Sigma (σ) Bond	Pi (π) Bond
Formation	Axial/Head-on overlap.	Lateral/Sidewise overlap.
Overlap Location	Along the internuclear axis.	Perpendicular to the internuclear axis.
Strength	Stronger.	Weaker.
Electron Cloud	Symmetrical and concentrated on the axis.	Two lobes above and below the axis.
Rotation	Free rotation is possible.	Restricts rotation.
Existence	Can exist independently.	Always present with a σ bond.
Orbitals Involved	s, p, and hybrid orbitals.	Primarily unhybridized p-orbitals.



Drawbacks of VBT

While VBT explains bond formation and directionality, it faced a problem: it predicted incorrect bond angles for molecules like methane (CH4), water, and ammonia. According to VBT using pure atomic orbitals, the three 2p orbitals of carbon (which are mutually perpendicular at 90°) should form bonds at 90°, not the observed 109.5°. To resolve this, Pauling introduced the concept of **orbital hybridization**.

Example: BF_3, $H_2C=CH_2$ (in C=C, one σ and one π bond).



- **Example: Boron Trifluoride (BF3)**
  B (ground state): $1s^2$, 2s2, $2px^1$. Only one unpaired electron.
  Promotion & Hybridization: Electron promoted from 2s to 2py. The 2s, 2px, and 2py orbitals hybridize to form three sp^2 orbitals in a trigonal plane. Each sp^2 orbital overlaps with a p orbital of F, forming three B-F σ bonds. The molecule is trigonal planar.
- **Example: Ethene (C2H4)**
  Each C atom undergoes sp^2 hybridization. Three sp^2 orbitals form σ bonds: two with H atoms and one with the other C atom. The unhybridized p orbitals on the two C atoms are parallel. They overlap sideways to form a ***π* bond**. Thus, the C=C double bond is one σ bond (sp^2-sp^2 overlap) and one π bond (p-p sideways overlap). The molecule is planar with H-C-H and H-C-C angles close to 120°.

sp^3 Hybridization:

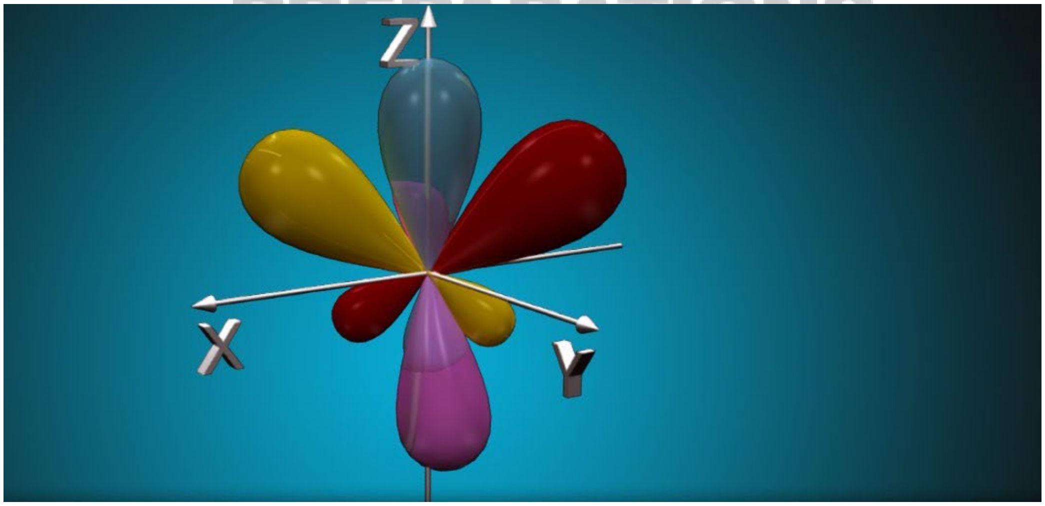
Orbitals Mixed: One s + three p orbitals.

Number of Hybrid Orbitals: 4 sp^3 orbitals.

Geometry: Tetrahedral.

Bond Angle: 109.5°.

Example: CH_4 (tetrahedral), NH_3 (pyramidal), H_2O (bent).



Example: $\overset{+}{NH_4}$ > NH_3 > $\overset{-}{NH_2}$

No L.P one LP two LP

If central atom different and attached atom same than B.A depends upon EN of central atom bond angle ∝ EN of central atom $H_3O^+ > NH_3 > PH_3$

If central atom same attached atom different then

$$\text{B.A} \propto \frac{1}{EN\ of\ attached\ atom}$$

Bond angle decreases → $SnCl_2 < SnBr_2 < SnI_2$ $because\ I_2$ **is less EN**

Topic-Wise One-Liners: Chemical Bonding

1. Introduction to Chemical Bonds

1. A **chemical bond** is the attractive force that holds atoms together in a molecule or compound.
2. The primary cause of bond formation is to achieve a **lower energy state** and greater stability.
3. The main types of chemical bonds are **Ionic, Covalent, and Metallic bonds**.
4. A **coordinate covalent bond** is a special type where both shared electrons are donated by a single atom.

2. Atomic Properties & Periodic Trends

5. **Atomic radius** is defined operationally (covalent/metallic/van der Waals radius), often taken as half internuclear distance

6. Across a period, atomic radius **decreases** due to an increase in effective nuclear charge.

7. Down a group, atomic radius **increases** due to the addition of new electron shells.

8. A **cation** is always smaller than its parent atom due to greater effective nuclear charge and reduced shielding.

9. An **anion** is always larger than its parent atom due to increased electron-electron repulsion.

10. For **isoelectronic species**, size decreases with increasing nuclear charge (e.g., $Al^{3+} < Mg^{2+} < Na^+ < Ne < F^- < O^{2-}$).

11. **Ionization Energy (IE)** is the minimum energy required to remove the most loosely bound electron from a gaseous atom.

12. Ionization energy generally **increases** across a period and **decreases** down a group.

13. **Exceptions** in IE trends: Group IIA (ns^2) has higher IE than Group IIIA (ns^2np^1), and Group VA (ns^2np^3) has higher IE than Group VIA (ns^2np^4).

14. **Electron Affinity (EA)** is the energy released when an electron is added to a neutral gaseous atom.

15. Electron affinity generally **increases** across a period and **decreases** down a group.

16. An exception to EA trend: **Chlorine has a higher electron affinity than Fluorine**.

17. **Electronegativity (EN)** is the ability of an atom to attract shared electrons in a covalent bond.

18. Electronegativity **increases** across a period and **decreases** down a group.

19. **Fluorine** is the most electronegative element on the Pauling scale.

3. Ionic Bond

20. An **ionic bond** is formed by the complete transfer of electrons from a metal to a non-metal.

21. Ionic bonds are favored by a **low ionization energy** of the metal and a **high electron affinity**(non-metals)

22. A large **electronegativity difference (usually >1.7)** is indicative of an ionic bond.

23. No bond is 100% ionic; for example, NaCl has =74 % ionic character.

24. Ionic compounds are **crystalline solids** with high melting and boiling points.

Practice MCQs

. Which overlapping may lead to Pi bond formation?

A) p-p in fluorine
B) s-p in hydrogen fluoride
C) sp^2-sp^2 in benzene
D) None

Correct Answer: D) None

2. Ionic bond with greater ionic character is mostly formed between elements of?

A) IA and IIA
B) IA and VIIA
C) IA and VIA
D) IIA and VIIA

Correct Answer: B) IA and VIIA

3. Bonds in calcium carbide between carbon atoms are?

A) Two pi
B) One sigma and one pi
C) One sigma and two pi
D) Ionic (no sigma, no pi)

Correct Answer: C) One sigma and two pi

4. Indicate the parameter which affects atomic radii in a period?

A) Number of shells
B) Nuclear charge
C) Shielding effect
D) Number of orbitals

Correct Answer: B) Nuclear charge

5. A cation is smaller in size than the parent atom because of?

A) Greater effective nuclear charge and lesser shielding effect
B) Greater effective nuclear charge and greater shielding effect
C) Lesser effective nuclear charge and lesser shielding effect
D) Lesser effective nuclear charge and greater shielding effect

Correct Answer: A) Greater effective nuclear charge and lesser shielding effect

6. Indicate the incorrect order of atomic/ionic radii?

A) $Na > Na^+$
B) $O^{2-} < O^-$
C) $Cl^- > Cl$
D) $Mg^{2+} < Mg$

Correct Answer: B) $O^{2-} < O^-$

7. Ionization energy of an element in a period increases due to?

A) Successive addition of electron shell
B) Successive increase of nuclear charge
C) Successive increase of effective nuclear charge
D) Both b and c

Correct Answer: D) Both b and c

8. In the formation of a compound AB, an electron is transferred from atom A to atom B, then?

A) A is divalent
B) B is oxidized and A is reduced
C) The compound AB is covalent
D) The compound AB is electrovalent

Correct Answer: D) The compound AB is electrovalent

9. In an ethylene molecule, the sigma bond is formed by ________ overlapping?

A) sp^3-sp^3
B) sp^2-sp^2
C) sp^3-sp
D) sp-sp^3

Correct Answer: B) sp^2-sp^2

10. Which of the following has the highest bond energy?

A) H–H bond in H_2
B) C–H in CH_4
C) N≡N bond in N_2
D) O=O bond in O_2

Correct Answer: C) N≡N bond in N_2

11. In which of the following molecules are triple covalent bonds present?

A) CH_4

Chemical Kinetics

Chemical Kinetics is the branch of chemistry that deals with the rates (or speeds) of chemical reactions, the factors affecting these rates, and the mechanisms by which reactions occur.

Rate of a Chemical Reaction

The rate of a reaction is defined as the change in the concentration of any reactant or product per unit time.

Explanation

During the course of a chemical transformation, reactant species are consumed as product species are generated. This process is quantitatively described by the continuous change in the concentrations of the involved substances. Specifically, the concentration of reactants exhibits a monotonic decrease, while the concentration of products shows a corresponding increase over time. This dynamic can be represented graphically. Consider an irreversible elementary reaction where a single reactant A is converted into a single product B: A → B. A plot of concentration versus time for such a system yields characteristic curves. The concentration of A, [A], will be represented by a downward-sloping curve that originates at the initial concentration, $[A]_0$, and asymptotically approaches zero. Conversely, the concentration of B, [B], will be represented by a rising curve that originates at zero and asymptotically approaches $[A]_0$ as the reaction goes to completion.

The slope of these concentration-time curves at any given instant is of paramount importance. At the very inception of the reaction (t=0), the slope of the curve for the reactant is at its steepest negative value, indicating the most rapid rate of consumption. Correspondingly, the slope for the product curve is at its steepest positive value, indicating the most rapid rate of formation. As the reaction progresses, these slopes become progressively less steep, demonstrating that the rate of the reaction is not constant but diminishes with time. This deceleration occurs because the frequency of successful molecular collisions decreases as the reactant concentration is depleted. Ultimately, the curve for the reactant will, in principle, intersect the time axis (concentration = 0), signifying the point of complete reaction, though for practical purposes, reactions may be considered complete when the concentration change becomes immeasurably small.

Mathematical Expression:

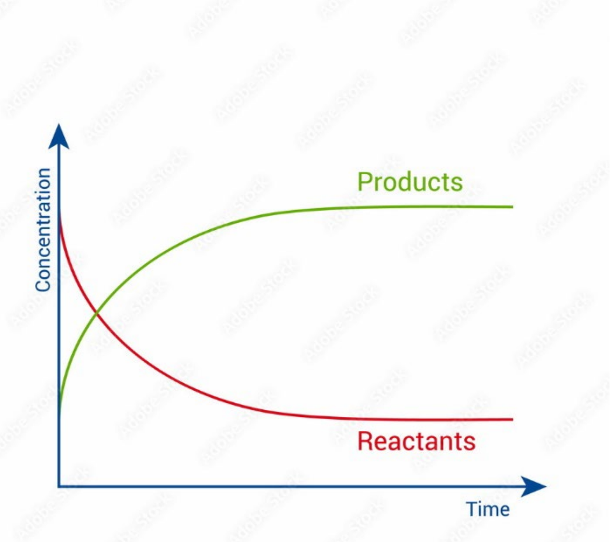
For a general reaction: $aA + bB \rightarrow cC + dD$

$$\text{Rate} = -\ (1/a)\ \Delta[A]/\Delta t = -\ (1/b)\ \Delta[B]/\Delta t = +\ (1/c)\ \Delta[C]/\Delta t = +\ (1/d)\ \Delta[D]/\Delta t$$

The negative sign for reactants indicates a decrease in concentration, while the positive sign for products indicates an increase.

Units: The unit of reaction rate is typically moles per cubic decimeter per second ($\text{mol dm}^{-3}\ \text{s}^{-1}$).

Graphical Representation:



A plot of concentration vs. time shows that the rate is not constant

The concentration of reactants decreases rapidly initially and then slowly.

The concentration of products increases rapidly initially and then slowly.

The **slope of the tangent** at any point on this curve gives the **instantaneous rate** at that moment.

Instantaneous Rate vs. Average Rate

Average Rate: The rate of reaction measured over a large time interval.

Average Rate = Δ(concentration) / Δ(time)

Instantaneous Rate: The rate of reaction at a specific moment in time. It is the rate when the time interval (Δt) approaches zero.

Instantaneous Rate = $-d[R]/dt = +d[P]/dt$ (where [R] is reactant and [P] is product concentration).

The instantaneous rate at the beginning of the reaction is the highest and decreases as the reaction proceeds.

Rate Law and Rate Constant

Rate Law (or Rate Equation): An experimentally determined expression that shows the relationship between the reaction rate and the concentrations of the reactants.

For a general reaction: $aA + bB \rightarrow \text{Products}$

Rate = $k[A]^m[B]^n$

Here, m and n are the **orders of the reaction** with respect to A and B, respectively. They are **not necessarily** related to the stoichiometric coefficients **a and b.**

Rate Constant (k): The quantitative relationship between the rate of a reaction and the concentrations of the reactants is codified in the **rate law**. This empirical law finds its historical roots in the **Law of Mass Action**, proposed by Guldberg and WaageThe proportionality constant k in the rate law.

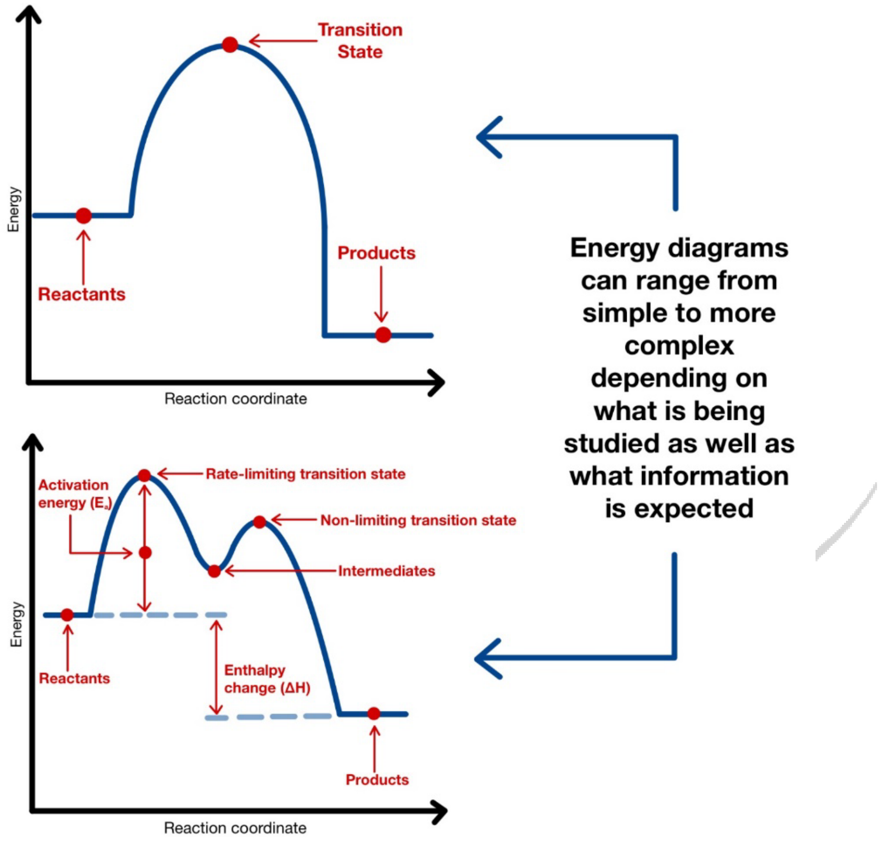
It is the rate of the reaction when the concentration of all reactants is unity (1 M).

It is constant for a given reaction at a specific temperature but changes with temperature.

Its units depend on the overall order of the reaction.

Activation Energy (E_a): The minimum amount of energy that colliding particles must possess for a reaction to occur. It is the energy barrier that must be overcome for reactants to transform into products.

Activated Complex (or Transition State): A temporary, high-energy, unstable species formed during the conversion of reactants to products. It has partial bonds and is the state of maximum potential energy in the reaction pathway.



Potential Energy Diagrams:

This diagram illustrate the energy changes during a reaction.

Exothermic Reaction: Products are at a lower energy level than reactants (ΔH is negative).

Endothermic Reaction: Products are at a higher energy level than reactants (ΔH is positive).

In both cases, the peak of the curve represents the activated complex, and the difference in energy between the reactants and this peak is the activation energy (E_a).

Factors Affecting Rate of Reaction

Nature of Reactants: Ionic reactions are generally much faster than covalent reactions because they involve simple ion exchange, while covalent reactions require bond breaking and forming.

Concentration of Reactants: According to the rate law, an increase in reactant concentration increases the reaction rate (except for zero-order reactions) because it increases the frequency of effective collisions.

ate ∝ $Z \cdot p \cdot e^{(-E_a/RT)}$ (Boltzmann fraction)where:

Z = Collision Frequency

p = Steric Factor (probability of correct orientation)

f = Fraction of molecules with energy ≥ E_a

Limitations of Collision Theory:

Applies mainly to simple gaseous reactions.

No method to calculate the steric factor (p) theoretically.

Ignores the contribution of vibrational and rotational energy.

Does not explain the cleavage and formation of bonds.

Transition State Theory (Activated Complex Theory)

This theory proposes that during a collision, reactant molecules form a short-lived, high-energy **activated complex** or **transition state**, which then decomposes to form products.

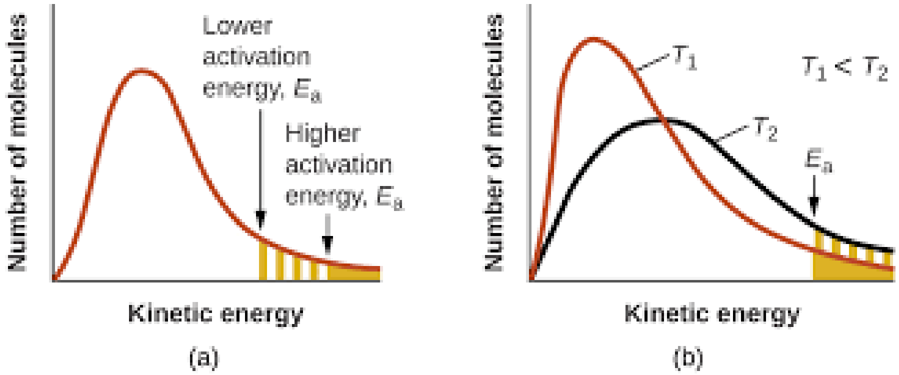
$$A + B\text{–}C \rightleftharpoons [A\text{---}B\text{---}C]^{\ddagger} \rightarrow A\text{–}B + C$$

(Reactants) (Activated Complex) (Products)

The double dagger (‡) denotes the transition state.

Effect of Temperature on Reaction Rate

The rate of most chemical reactions increases with temperature. A rough rule is that the rate doubles for every 10°C rise in temperature.



(a) (b)

Arrhenius Equation

The Arrhenius equation gives the quantitative relationship between the rate constant (k), temperature (T), and activation energy (E_a).

$k = A\, e^{(-E_a/RT)}$

k = rate constant

A = Arrhenius constant or frequency factor (related to collision frequency and orientation)

E_a = Activation Energy (in J mol^{-1})

R = Universal Gas Constant (8.314 J mol^{-1} K^{-1})

T = Temperature in Kelvin

The logarithmic form is more useful for calculating E_a:

$\ln k = \ln A^{-} (E_a / RT)$ or $\log k = \log A^{-(E_a / 2.303RT)}$

Topic-wise One-Liners: Chemical Kinetics

1. Introduction to Chemical Kinetics

1. **Chemical Kinetics** is the branch of chemistry that deals with the study of reaction rates and their mechanisms.
2. The **rate of a reaction** is defined as the change in concentration of a reactant or product per unit time.
3. For a reaction, $aA + bB \rightarrow cC + dD$, the rate is expressed as: Rate = $-(1/a)\, \Delta [A]/\Delta t = -(1/b)\, \Delta[B]/\Delta t = +(1/c)\, \Delta[C]/\Delta t = +(1/d)\, \Delta[D]/\Delta t$.
4. The unit of reaction rate is typically **$mol\ dm^{-3}\ s^{-1}$**.
5. The **average rate** is the change in concentration over a finite time interval.
6. The **instantaneous rate** is the rate at a specific moment, given by the slope of the tangent on a concentration-time graph.
7. The instantaneous rate is highest at the start of the reaction and decreases over time.

2. Rate Law and Rate Constant

8. The **Rate Law** is an experimentally determined expression relating the reaction rate to the concentrations of reactants.

9. For a reaction $aA + bB \rightarrow$ products, the rate law is **$Rate = k\,[A]^m\,[B]^n$**.

10. The exponent's **m** and **n** are the **orders of the reaction** with respect to A and B, respectively.

11. The **overall order** of a reaction is the sum of the powers $(m + n)$.

12. The **rate constant (k)** is the proportionality constant in the rate law.

13. The value of **k** is constant for a given reaction at a specific temperature.

14. The units of the rate constant **k** depend on the overall order of the reaction.

3. Order of Reaction

15. A **zero-order reaction** has a rate independent of reactant concentration (Rate = k).

16. The half-life ($t_{1/2}$) for a zero-order reaction is directly proportional to the initial concentration **$t_{1/2} = [A]^0 / (2k)$**

17. A **first-order reaction** has a rate directly proportional to the concentration of a single reactant (Rate = k [A]).

18. The half-life for a first-order reaction is constant and independent of the initial concentration ($t_{1/2} = 0.693/k$).

19. A **second-order reaction** has a rate proportional to the square of a single reactant's concentration or to the product of two reactant concentrations.

20. The half-life for a second-order reaction (with $2A \rightarrow$ products) is inversely proportional to the initial concentration **($t_{1/2} = 1 / (k\,[A]_0)$).**

21. A **pseudo-first-order reaction** is a higher-order reaction that behaves as first-order because one reactant is in large excess.

4. Molecularity of a Reaction

22. **Molecularity** is defined as the number of reactant molecules, atoms, or ions colliding in an **elementary reaction**.

23. An elementary reaction can be **unimolecular** (one reactant), **bimolecular** (two reactants), or **termolecular** (three reactants).

24. **Molecularity** is always a whole number and is theorized from the reaction mechanism.

25. **Order** is an experimental quantity that can be fractional, while **molecularity** is a theoretical

Practice MCQs

Q1. The branch of chemistry dealing with reaction rates and mechanisms is called:
A) Thermodynamics
B) Electrochemistry
C) Chemical Kinetics
D) Stereochemistry
Correct Answer: C) Chemical Kinetics

Q2. For the reaction $2N_2O_5 (g) \rightarrow 4NO_2 (g) + O_2 (g)$, if the rate of formation of O_2 is 2.5×10^{-4} mol L^{-1} s^{-1}, the rate of disappearance of N_2O_5 is:
A) 2.5×10^{-4} mol L^{-1} s^{-1}
B) 5.0×10^{-4} mol L^{-1} s^{-1}
C) 1.25×10^{-4} mol L^{-1} s^{-1}
D) 1.0×10^{-3} mol L^{-1} s^{-1}
Correct Answer: B) 5.0×10^{-4} mol L^{-1} s^{-1}

Q3. The unit of the rate constant for a zero order reaction is:
A) s^{-1}
B) L mol^{-1} s^{-1}
C) mol L^{-1} s^{-1}
D) L^2 mol^{-2} s^{-1}
Correct Answer: C) mol L^{-1} s^{-1}

Q4. For a first order reaction, the half-life is 20 minutes. The time required for the concentration to drop from 1.0 M to 0.125 M is:
A) 20 min
B) 40 min
C) 60 min
D) 80 min
Correct Answer: C) 60 min

Q5. A plot of ln[A] versus time gives a straight line with a negative slope. The order of the reaction is:
A) Zero
B) First
C) Second
D) Third
Correct Answer: B) First

Q6. The hydrolysis of ethyl acetate in the presence of a large excess of water is an example of:
A) Zero order reaction
B) First order reaction
C) Pseudo-first order reaction
D) Second order reaction
Correct Answer: C) Pseudo-first order reaction

Q7. The molecularity of the elementary step $2NO + O_2 \rightarrow 2NO_2$ is:
A) 1
B) 2
C) 3
D) 4
Correct Answer: C) 3

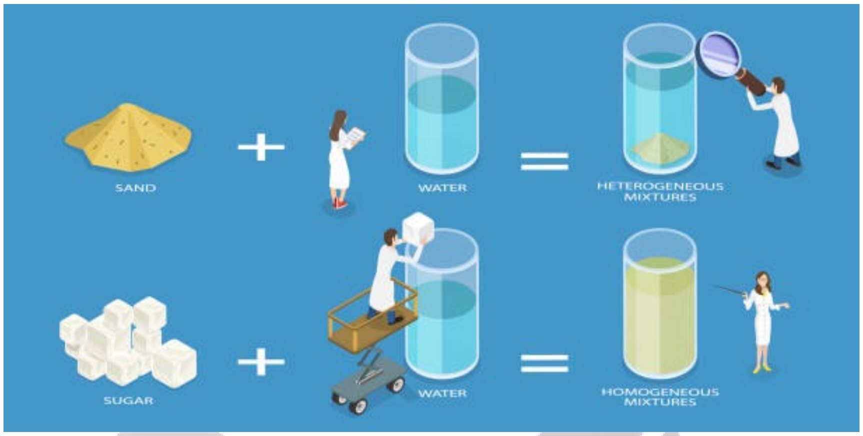
Q8. Which of the following is TRUE for order and molecularity?
A) Both are always the same
B) Order can be fractional, molecularity cannot
C) Molecularity is experimental, order is theoretical
D) They are identical for complex reactions
Correct Answer: B) Order can be fractional, molecularity cannot

Q9. The rate law for a reaction is found to be Rate = $k [A]^1[B]^{1/2}$. The overall order of the reaction is:
A) 1
B) 1.5
C) 2
D) 2.5
Correct Answer: B) 1.5

Q10. In the decomposition of H_2O_2, the volume of O_2 evolved is measured. If V∞ is the final volume and V~t~ is the volume at time t, for a first order reaction:
A) k = (2.303/t) log(V∞/Vt)
B) k = (2.303/t) log(V∞/(V∞ - Vt))
C) k = (1/t) (Vt/(V∞ - Vt))

Solutions and Colloids

Introduction to Solutions



Definition:
A solution is a homogeneous Mixture of two or more substances on a molecular or ionic level. The composition and properties are uniform throughout the mixture.

Components:

Solute: The substance present in a smaller quantity, which gets dissolved.

Solvent: The substance present in a larger quantity, which does the dissolving.

Concentration: The amount of solute dissolved in a given amount of solvent or solution. A solution with a low concentration is **dilute**, while one with a high concentration is **concentrated**.

Solubility: The maximum amount of solute that can be dissolved in a fixed amount of solvent at a specific temperature and pressure to form a saturated solution.

Types of Solutions

Solutions can be classified based on the physical state of the solute and solvent.

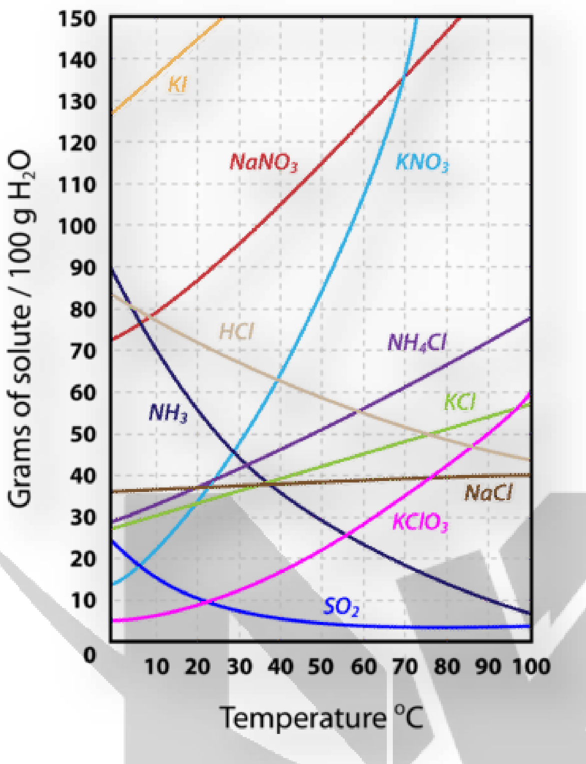
Solute	Solvent	Example
Gas	Gas	Air (Mixture of N_2, O_2, etc.)
Gas	Liquid	CO_2 in water (Carbonated drinks), O_2 in water
Gas	Solid	H_2 adsorbed by Palladium
Liquid	Gas	Water vapor in air (Humidity)
Liquid	Liquid	Alcohol in water, Benzene in Toluene
Liquid	Solid	Mercury in Silver (Amalgam),
Solid	Liquid	Sugar in water, Salt in water
Solid	Gas	Dust in air,Carbon black in air
Solid	Solid	Metal alloys (e.g., Copper in Zinc - Brass), Carbon in Iron (Steel),pearl etc

Concentration Units of Solutions

The concentration of a solution can be expressed in several ways:

Percentage Composition

Solubility Curves



A graph of solubility (y-axis) vs. temperature (x-axis).

Continuous Curves: Show a smooth change in solubility without any abrupt breaks (e.g., KNO_3, NaCl).

Discontinuous Curves: Show a sharp break where a new solid phase with different hydration appears (e.g., Na_2SO_4, $CaCl_2$).

Solutions of Liquids in Liquids

Completely Miscible Liquids

Liquids that mix in all proportions to form a single homogeneous phase.

Examples: Ethanol and water, Benzene and Toluene.

Partially Miscible Liquids

Liquids that dissolve in each other only to a limited extent. Beyond this limit, they form two separate layers, each being a saturated solution of one liquid in the other. These are called **conjugate solutions**.

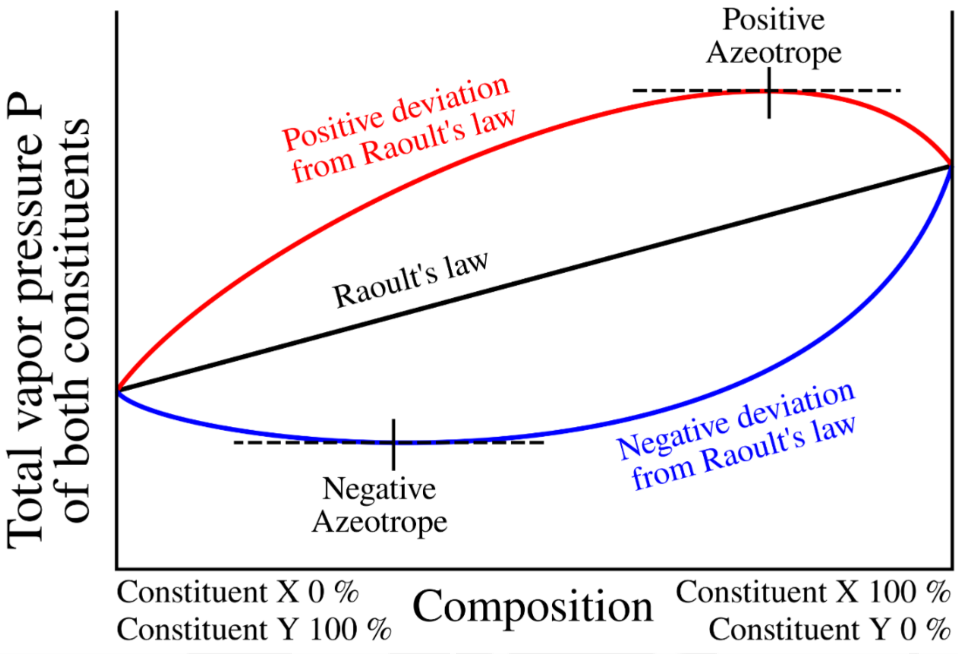
Examples:

Phenol-Water System: At room temperature, they form two layers. On heating, the mutual solubility increases until a temperature called the **Critical Solution Temperature (CST)** or **Upper Consolute Temperature** is reached (65.9°C for phenol-water), above which the liquids are completely miscible.

Triethylamine-Water System: Shows a **Lower Consolute Temperature**, below which the liquids are completely miscible.

Nicotine-Water System: Shows both upper and lower **Consolute** temperatures, forming a closed solubility loop.

Negative Deviation: Solute-solvent interactions are stronger than the pure interactions (e.g., hydrogen bonding). Total vapour pressure is lower than that predicted by Raoult's law. E.g., Chloroform-Acetone, HNO_3-Water.



Azeotropes

Azeotropes (or azeotropic mixtures) are liquid mixtures that distill at a constant temperature without any change in composition, behaving like a pure substance. They are **mixtures, not compounds**, because their composition changes if the total pressure is altered. Azeotropes arise from significant deviations from Raoult's law and pose a limit to separation by simple fractional distillation.

Minimum Boiling Azeotrope: Formed by solutions showing strong positive deviation. The boiling point of the azeotrope is lower than the boiling points of either pure component. The vapor-pressure vs. composition curve has a maximum, leading to a minimum in the boiling point vs. composition diagram. The most famous example is the ethanol-water azeotrope, which boils at 78.1°C and contains approximately 95.6% ethanol and 4.4% water by mass. It is impossible to obtain 100% ethanol by distilling a dilute ethanol-water solution; the distillate will be this azeotrope.

Maximum Boiling Azeotrope: Formed by solutions showing strong negative deviation. The boiling point of the azeotrope is higher than the boiling points of either pure component. The vapor-pressure curve has a minimum. An example is hydrochloric acid-water, which forms an azeotrope at 110°C containing about 20.2% HCl.

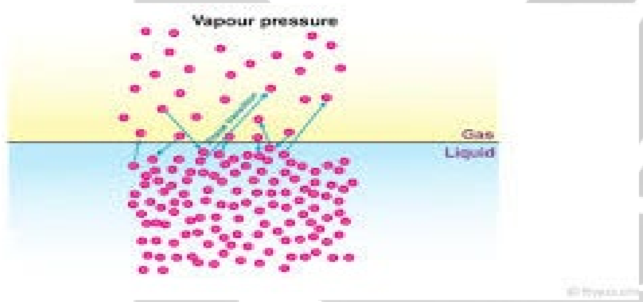
Fractional Distillation

This is a process used to separate a mixture of two or more miscible liquids whose boiling points differ by less than 25-30°C. It employs a fractionating column, which provides multiple vaporization-condensation cycles (theoretical plates).

For Ideal Solutions and Zeotropic Mixtures: These mixtures change composition upon boiling (the vapor is richer in the more volatile component). As vapors ascend the column, they repeatedly condense and re-vaporize. With each cycle, the vapor becomes progressively enriched in the lower-boiling component, which is collected at the top. The less volatile component remains mostly in the still pot. Complete separation into pure components is theoretically possible with a sufficiently efficient column. Benzene-toluene is a classic example.

For Azeotropic Mixtures: Fractional distillation cannot break the azeotrope. Distilling a mixture of composition other than the azeotropic composition will yield the azeotrope as the distillate, leaving one of the pure components behind. For example, distilling a 50% ethanol-water mixture yields the 95.6% azeotrope as the distillate, leaving almost pure water in the pot. To obtain pure ethanol beyond the azeotropic composition, methods like azeotropic distillation (adding a third component like benzene to form a new, lower-boiling ternary azeotrope) or molecular sieves are used.

Colligative Properties



Definition

Colligative properties are those properties of dilute solutions that depend solely on the **number** of solute particles (ions or molecules) present in a given amount of solvent and **not on their chemical identity**. They arise from the lowering of the chemical potential of the solvent due to the presence of solute. The four primary colligative properties are applicable to

1. **Ideal dilute solutions**
2. **Containing non-volatile,**
3. **Non-electrolyte solutes.**

The Four Colligative Properties

1. Lowering of Vapour Pressure:

As explained by Raoult's Law: $\Delta P / P^\circ = X_2$

This is the fundamental colligative property from which the others are derived.

2. Elevation of Boiling Point (ΔTb)

Boiling occurs when the vapor pressure of a liquid equals the external atmospheric pressure. Adding a non-volatile solute lowers the vapor pressure of the solvent. Therefore, a higher temperature is required for the solution's vapor pressure to reach the external pressure. The elevation is given by:

$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = K_b \times m$

where m is the molality of the solution, and Kb is the **molal elevation constant** or **ebullioscopic**

Topic-wise One-Liners: Solutions and Collides

1.0 Concept of a Solution

1. A **solution** is a homogeneous mixture of two or more substances on a molecular or ionic level.
2. The component present in a larger amount is called the **solvent**.
3. The component present in a smaller amount is called the **solute**.
4. Every sample of matter with uniform properties and fixed composition is called a **phase**.
5. A **binary solution** is a mixture containing two substances.
6. The amount of solute dissolved in a unit volume of solution or solvent is termed as **concentration**.
7. Solutions with relatively low solute concentration are called **dilute solutions**.
8. Solutions with relatively high solute concentration are called **concentrated solutions**.

2.0 Concentration Units

9. **Percentage weight/weight (% w/w)** is the mass of solute per 100 parts by mass of solution.
10. **Percentage weight/volume (% w/v)** is the mass of solute per 100 parts by volume of solution.
11. **Percentage volume/volume (% v/v)** is the volume of solute per 100 parts by volume of solution.
12. **Molarity (M)** is defined as the number of moles of solute dissolved per dm^3 (litre) of the solution.
13. Molarity is **temperature-dependent** because volume changes with temperature.
14. **Molality (m)** is defined as the number of moles of solute per kilogram (1000 g) of the solvent.
15. Molality is **temperature-independent** because it involves mass, which does not change with temperature.
16. **Mole Fraction** is the ratio of the number of moles of a component to the total number of moles of all components in the solution.
17. The sum of the mole fractions of all components in a solution is always equal to **one**.
18. **Parts Per Million (ppm)** is defined as the number of parts of solute per million parts of the solution.
19. Ppm is used for expressing very low concentrations, such as impurities in water.
20. **Normality (N)** is the number of gram equivalents of solute per litre of solution.

3.0 Types of Solutions

21. Solutions can be classified into nine types based on the physical state of the solute and solvent.
22. **Example of Gas in Gas:** Air (a mixture of N_2, O_2, etc.).
23. **Example of Gas in Liquid:** Oxygen in water, CO_2 in water (carbonated drinks).
24. **Example of Gas in Solid:** Hydrogen adsorbed by palladium.
25. **Example of Liquid in Gas:** Water vapor in air (humidity), fog.
26. **Example of Liquid in Liquid:** Alcohol in water, benzene in toluene.
27. **Example of Liquid in Solid:** Mercury in silver (amalgam),
28. **Example of Solid in Liquid:** Sugar in water, salt in water.
29. **Example of Solid in Gas:** Dust or iodine vapor in air.
30. **Example of Solid in Solid:** Metal alloys like brass (copper in zinc) and steel (carbon in iron).

4.0 Solubility and Factors Affecting It

31. **Solubility** is the maximum amount of solute that can be dissolved in a fixed amount of solvent at a specific temperature to form a saturated solution.
32. In a **saturated solution**, a dynamic equilibrium exists: Rate of Dissolution = Rate of Crystallization.
33. A **supersaturated solution** contains more solute than a saturated solution at the same temperature

Practice MCQs

1. A solution is defined as a:
A) Heterogeneous mixture of two or more substances
B) Homogeneous mixture of two or more substances on a molecular level molecular or ionic level
C) Mixture where the solute is always a solid
D) Mixture where the solvent is always water
Correct Answer: B) Homogeneous mixture of two or more substances on a molecular level or ionic level.

2. The component of a solution present in a smaller amount is called the:
A) Solvent
B) Solution
C) Solute
D) Phase
Correct Answer: C) Solute

3. In a solution, the component present in larger amount is called:
A) Solute
B) Solvent
C) Colloid
D) Suspension
Correct Answer: B) Solvent

4. A solution with a relatively low concentration of solute is termed:
A) Saturated
B) Concentrated
C) Dilute
D) Supersaturated
Correct Answer: C) Dilute

5. Which concentration unit is expressed as the number of moles of solute per litre of solution?
A) Molality
B) Mole fraction
C) Molarity
D) Normality
Correct Answer: C) Molarity

6. Which of the following concentration units is temperature-dependent?
A) Molality
B) Mole fraction
C) Molarity
D) Percentage by weight
Correct Answer: C) Molarity

7. The number of moles of solute per kilogram of solvent is called:
A) Molarity
B) Molality
C) Normality
D) Mole fraction
Correct Answer: B) Molality

8. The sum of the mole fractions of all components in a solution is always equal to:
A) Zero
B) One
C) One hundred
D) The molarity
Correct Answer: B) One

9. Which unit is used to express the concentration of very dilute solutions, such as impurities in water?
A) Molarity
B) Molality
C) Parts per million (ppm)
D) Normality
Correct Answer: C) Parts per million (ppm)

10. Which of the following is NOT a concentration unit?
A) Molarity
B) Molality
C) Mole fraction
D) Boiling point
Correct Answer: D) Boiling point

11. Which of the following is NOT a method to express concentration?
A) Percentage by mass
B) Molarity
C) Pressure

Electrochemistry

Introduction to Electrochemistry

Electrochemistry is the branch of chemistry that deals with the interconversion of chemical energy and electrical energy. This involves two main types of processes:

Production of Electricity from Chemical Reactions: This occurs in **Galvanic or Voltaic Cells** (like batteries), where a spontaneous redox reaction generates an electric current.

Use of Electricity to Drive Chemical Reactions: This occurs in **Electrolytic Cells**, where an external electric current is used to force a non-spontaneous chemical reaction to occur, a process known as **electrolysis**.

A fundamental requirement for these processes is the presence of an **electrolyte**—a substance that in solution or molten state conducts electricity by the movement of ions.

Oxidation and Reduction (Redox Reactions)

Basic Concepts

The concepts of oxidation and reduction are central to electrochemistry. Historically, these terms were defined in relation to oxygen and hydrogen transfer. Oxidation was described as the gain of oxygen or the loss of hydrogen by a substance. Reduction was conversely defined as the loss of oxygen or the gain of hydrogen. While these definitions are still useful for certain reactions, the modern, more comprehensive understanding is based on electron transfer.

Classical Concept:

Oxidation: Addition of oxygen or removal of hydrogen.

$2SO_2+O_2\rightarrow 2SO_3$ (Oxidation of SO_2)

Reduction: Removal of oxygen or addition of hydrogen.

$H_2+Cl_2\rightarrow 2HCl$ (Reduction of Cl_2)

Electron Transfer Concept (Modern Concept):

It defines oxidation and reduction in terms of electrons. Oxidation is the loss of electrons by a species, resulting in an increase in its oxidation state. Reduction is the gain of electrons, leading to a decrease in oxidation state. Crucially, these processes occur simultaneously in what is known as a **redox reaction**; one species is oxidized (the reducing agent) while another is reduced (the oxidizing agent). The electrons lost by the oxidized species are directly gained by the reduced species. This electron-transfer framework provides a universal language for analyzing reactions in aqueous solution, molten salts, and even in solid-state chemistry.

Redox Reaction: A reaction in which oxidation and reduction occur simultaneously.

Oxidation State (Oxidation Number)

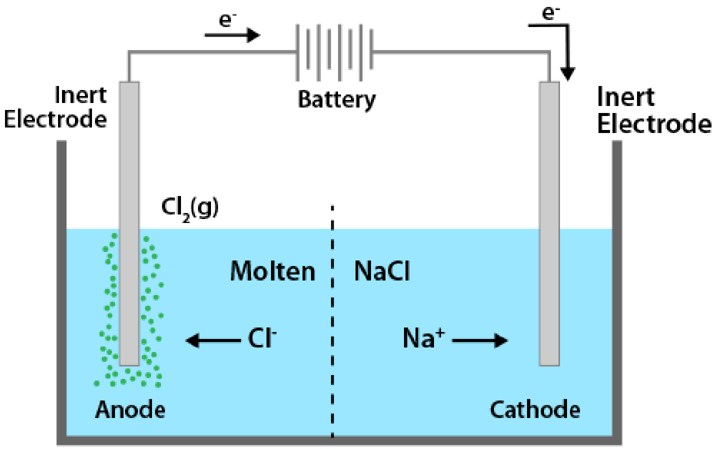
The oxidation number (or oxidation state) is a conceptual tool used to keep track of electron transfer in redox reactions. It is defined as the **apparent charge an atom** would carry if all its bonds to different atoms were considered 100% ionic, disregarding covalent character. Assigning oxidation numbers follows a set of well-established rules, which are essential for balancing redox equations and identifying oxidizing and reducing agents.

Rules for Assigning Oxidation Numbers:

The oxidation number of an atom in a **free element** is **0** (e.g. O_2, Zinc)

The oxidation number of a **monatomic ion** is equal to its **charge** like **Na^+**

Thus, electrolysis decomposes hydrochloric acid into its constituent elements.



Applications of Electrolysis

Applications of Electrolysis

The principles of electrolysis have vast industrial and technological applications:

1. **Electroplating:** The process of depositing a thin, coherent layer of a superior metal (e.g., Cr, Ni, Ag, Au) onto an inferior metal object. The object to be plated is made the cathode, a strip of the plating metal is the anode, and a solution of a salt of the plating metal serves as the electrolyte. This is used for decoration, corrosion resistance, and improving surface properties.
2. **Purification of Metals:** Impure metals can be refined electrolytically. For copper, a thick slab of impure copper is made the anode, a thin sheet of pure copper is the cathode, and acidified copper (II) sulphate is the electrolyte. On passing current, copper from the anode dissolves ($Cu \rightarrow Cu^{2+} + 2e^-$), and pure copper deposits on the cathode ($Cu^{2+} + 2e^- \rightarrow Cu$). Impurities either dissolve into the solution or fall to the bottom as "anode mud," which often contains valuable metals like gold and silver.
3. **Extraction of Metals:** Highly reactive metals that cannot be reduced by carbon (e.g., Na, K, Mg, Al) are extracted from their molten ores or salts via electrolysis. For example, **aluminium** is extracted from purified alumina (Al_2O_3) dissolved in molten **cryolite (Na_3AlF_6)** via the **Hall-Héroult process.**
4. **Manufacture of Chemicals:** Several important industrial chemicals are produced electrolytically.
5. **Chlor-alkali industry:** Electrolysis of concentrated brine (NaCl solution) produces chlorine gas at the anode, hydrogen gas at the cathode, and sodium hydroxide (NaOH) in the solution.
6. **Heavy water (D_2O):** Can be produced by the prolonged electrolysis of water, as H_2 is evolved slightly faster than D_2 (from HDO), enriching the remaining water in deuterium.
7. **Anodizing:** A process to increase the thickness of the natural oxide layer on the surface of metals like aluminium. The metal is made the anode in an electrolytic bath (e.g., sulfuric acid). Oxygen generated at the anode reacts with the metal to form a durable, corrosion-resistant oxide coating that can also be dyed.

Electrical Conductance of Electrolytic Solutions

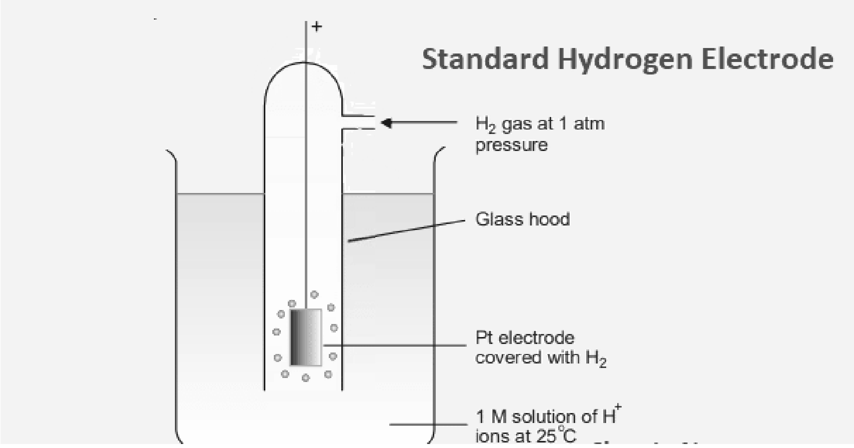
Key Definitions and Units

Resistance (R): Opposition to current flow. Unit: **Ohm (Ω)**.

Conductance (G): Reciprocal of resistance. G=1/R. Unit: **Siemens (S) or Ohm−1**

The standard electrode potential of SHE is **arbitrarily assigned a value of 0.00 V**

Half-reactions:



When SHE acts as anode: $H_2\,(g) \rightarrow 2H\,(aq)^+ + 2e^-$ ($E_{Ox} = 0$)

When SHE acts as cathode: $2H\,(aq)^+ + 2e^- \rightarrow H_2\,(g)$ ($E_{red} = 0$)

Standard Electrode Potential (E°)

The potential of an electrode when it is in contact with a 1M solution of its ions at 298 K and 1 atm pressure, measured relative to the SHE.

Measurement of Electrode Potential

The electrode whose potential is to be measured is connected to the SHE to form a galvanic cell. The potential difference measured by the voltmeter gives the standard electrode potential of that electrode directly.

Example: For a Zn electrode, $E_{red} = -0.76$V this means Zn has a lower tendency to gain electrons (be reduced) compared to hydrogen.

Electrochemical Series (ECS)

The Electrochemical Series is an arrangement of elements in the **order of increasing standard reduction potentials**.

Key Features and Applications

1. **Predicting the Direction of Redox Reactions:** A redox reaction is spontaneous (produces a positive EMF in a galvanic cell) if the species with the **higher (more positive) reduction potential** is reduced, and the species with the **lower (more negative) reduction potential** is oxidized. For example, Zn ($E° = -0.76$ V) reduces Cu^{2+} ($E° = +0.34$ V) spontaneously: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$.
2. **Relative Strengths of Oxidizing and Reducing Agents:** Li^+/Li ($E° = -3.04$ V) is a very weak oxidizing agent but Li metal is the strongest reducing agent in aqueous solution. F_2/F^- ($E° = +2.87$ V) is the strongest oxidizing agent.
3. **Displacement Reactions:** A metal higher in the series (more negative E°) can displace a metal lower in the series from its salt solution. Zn displaces Cu from $CuSO_4$, but Cu cannot displace Zn from $ZnSO_4$.
4. **Displacement of Hydrogen from Acids:** Metals with negative reduction potentials (above hydrogen in the series, $E° < 0$) can displace H_2 from dilute acids (H^+ is reduced to H_2). Metals with positive potentials (below hydrogen) cannot.

5. **Predicting Feasibility of Corrosion:** Metals with negative E° values (like Fe, Zn) are thermodynamically prone to oxidation (corrosion) in the presence of air and moisture. Noble metals with positive E° (like Au, Pt) are resistant.
6. **Calculation of Standard EMF of a Cell:** For a galvanic cell, the standard EMF (E°$_{cell}$) is given by: **E°$_{cell}$ = E°$_{Cathode}$- E°$_{Anode}$**where E°$_{cathode}$ is the reduction potential of the cathode half-cell and E°$_{anode}$ is the reduction potential of the anode half-cell. Since oxidation occurs at the anode, if using reduction potentials, E°$_{anode}$ is the reduction potential of the species being oxidized. For the Daniell cell: E°$_{cell}$ = E°(Cu^{2+}/Cu) - E°(Zn^{2+}/Zn) = 0.34 - (-0.76) = **+1.10 V**.

Cell Potential and Nernst Equation

Cell Potential (EMF, E°cell)

The potential difference between the two electrodes of a galvanic cell under standard conditions (1 M concentration, 1 atm pressure, 298 K) when no current is flowing.

Formula: E°cell = E°cathode − E°anode

Spontaneity: A **positive E°cell** indicates a spontaneous reaction.

Example: Calculating E°cell for a Zn-Cu Cell

Given: E°(Zn^{2+}/Zn) = -0.76 V; E°(Cu^{2+}/Cu) = +0.34 V

E°cell = E°(Cu^{2+}/Cu) − E°(Zn^{2+}/Zn) = 0.34 V − (-0.76 V) = **1.10 V**

Cell Representation (Cell Notation)

Anode (oxidation) is written on the **left**.

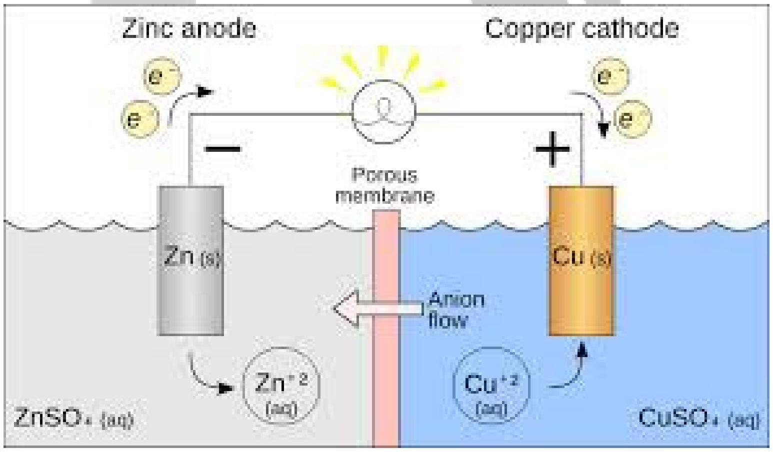
Cathode (reduction) is written on the **right**.

| represents a phase boundary (e.g., between solid electrode and ion solution).

|| represents the salt bridge.

Example (Daniel Cell): Zn(s) | Zn^{2+}(1 M) || Cu^{2+}(1 M) | Cu(s)

Nernst Equation



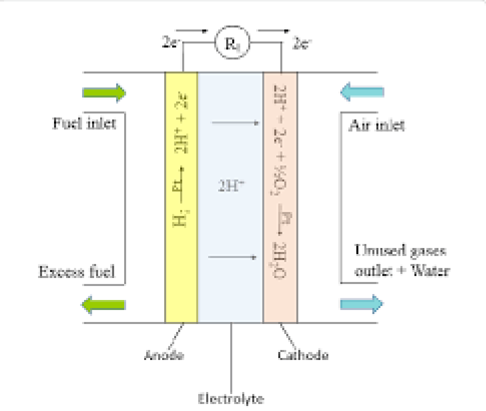
Nernst Equation

Relates the cell potential under non-standard conditions to the standard potential and the reaction quotient (Q).

For a general half-reaction: $aA + ne^- \rightleftharpoons bB$

General Form: E = E° − (RT / nF) ln (Q)

- **Hydrogen-Oxygen Fuel Cell:** The most developed type, used in space missions and prototype vehicles.
  Electrodes: Porous graphite/nickel electrodes impregnated with catalysts (Pt, Pd).
  Electrolyte: Aqueous KOH solution (alkaline) or a solid polymer electrolyte.
  Reactions (in Alkaline Medium):
  Anode (Oxidation): $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$
  Cathode (Reduction): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
  Overall: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
  Advantages: High efficiency (60-75%, compared to 40% for heat engines), only water as by-product (pollution-free), quiet operation.
  Disadvantages: High cost due to precious metal catalysts, requires pure hydrogen (storage and distribution challenges), durability issues.
  Other types include methanol fuel cells, phosphoric acid fuel cells, and molten carbonate fuel cells.
  Overall: $2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$



Advantages: High efficiency Upto 75% only water produced.
Disadvantages: High cost, requires pure hydrogen and oxygen.

Corrosion and Its Prevention

Corrosion

Corrosion is the undesired, gradual, and electrochemical deterioration of a metal by its reaction with the environment (oxygen, water, acids). The most common example is the rusting of iron.

Mechanism of Rusting of Iron: Rust is a hydrated form of iron(III) oxide, $Fe_2O_3 \cdot xH_2O$. Rusting requires both oxygen and water (or moisture) and is accelerated by electrolytes (e.g., salts). It occurs via the formation of tiny galvanic cells on the iron surface (heterogeneous composition, stress points, impurities act as cathodes).

Anodic Areas (Oxidation): $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$. The electrons flow through the metal.

Cathodic Areas (Reduction): In neutral/alkaline conditions: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$.

The Fe^{2+} and OH^- ions diffuse and meet, forming $Fe(OH)_2$, which is further oxidized by oxygen to $Fe(OH)_3$ and then dehydrates to rust.

Prevention Methods

1. **Barrier Protection:** Isolating the metal from the environment using paint, grease, oil, plastic coating, or enamel.

Topic-wise One-Liner Statements: Electrochemistry

1. Introduction to Electrochemistry

1. **Electrochemistry** is the branch of chemistry dealing with the interconversion of electrical energy and chemical energy.
2. An **electrolytic cell** uses electrical energy to drive a non-spontaneous chemical reaction (electrolysis).
3. A **galvanic** or **voltaic cell** converts chemical energy from a spontaneous reaction into electrical energy.

2. Oxidation and Reduction (Redox)

4. **Oxidation** is defined as the loss of electrons or an increase in oxidation number.
5. **Reduction** is defined as the gain of electrons or a decrease in oxidation number.
6. An **oxidizing agent** accepts electrons and gets reduced during a reaction.
7. A **reducing agent** donates electrons and gets oxidized during a reaction.
8. In the classical concept, oxidation is the addition of oxygen or removal of hydrogen.
9. In the classical concept, reduction is the removal of oxygen or addition of hydrogen.

3. Oxidation State (Oxidation Number)

10. The **oxidation number** is the apparent charge an atom would have if all bonds were 100% ionic.
11. The oxidation number of a free element (e.g., Na, O_2, Cl_2) is always zero.
12. The oxidation number of hydrogen is +1, except in metal hydrides (e.g., NaH, CaH_2) where it is -1.
13. The oxidation number of oxygen is -2, except in peroxides (e.g., H_2O_2) where it is -1, and in OF_2 where it is +2.
14. The algebraic sum of oxidation numbers of all atoms in a neutral molecule is zero.
15. The algebraic sum of oxidation numbers of all atoms in a polyatomic ion is equal to the charge on the ion.
16. In $K_2Cr_2O_7$, the oxidation number of Cr is +6.
17. In H_2SO_4, the oxidation number of S is +6.

4. Balancing Redox Reactions

18. The **Oxidation Number Method** balances redox reactions by equating the total increase and decrease in oxidation numbers.
19. The **Ion-Electron (Half-Reaction) Method** splits the reaction into oxidation and reduction half-reactions, which are balanced separately before combining.
20. In the half-reaction method for acidic medium, O atoms are balanced by adding H_2O and H atoms are balanced by adding H^+ ions.
21. In the half-reaction method for basic medium, O atoms are balanced by adding H_2O, and H atoms are balanced by adding OH^- ions.

5. Electrolytes and Electrolytic Conduction

22. An **electrolyte** is a substance that in solution or molten state conducts electricity by the movement of ions.
23. A **strong electrolyte** is completely ionized in solution (e.g., NaCl, H_2SO_4, NaOH).
24. A **weak electrolyte** is partially ionized in solution (e.g., CH_3COOH, NH_4OH).
25. **Electrolysis** is the process of chemical decomposition of an electrolyte by the passage of electric

Practice MCQs

1. Weak electrolyte in solution is:

A) completely ionized

B) slightly ionized

C) never ionized

D) destroyed

Correct Answer: B) slightly ionized

2. Which one of the following is a strong electrolyte in solution?

A) Ammonium hydroxide

B) Carbonic acid

C) Potassium iodide

D) Acetic acid

Correct Answer: C) Potassium iodide

3. In an electrolytic cell, the cathode has a charge:

A) Positive

B) Negative

C) Neutral

D) Zero

Correct Answer: B) Negative

4. The oxidation number of Cl in $HClO_3$ is:

A) -1

B) +1

C) +3

D) +5

Correct Answer: D) +5

5. The oxidation number of magnesium in $MgCO_3$ is:

A) +3

B) +2

C) +1

D) -1

Correct Answer: B) +2

6. Which one of the following is a reduction reaction?

A) $Br_2 \rightarrow 2Br^-$

B) $Fe^{2+} \rightarrow Fe^{3+}$

C) $Zn \rightarrow Zn^{2+}$

D) $Sn^{2+} \rightarrow Sn^{4+}$

Correct Answer: A) $Br_2 \rightarrow 2Br^-$

7. A cell in which a non-spontaneous redox reaction is carried out by passing an electric current is a/an:

A) Galvanic cell

B) Voltaic cell

C) Daniell cell

D) Electrolytic cell

Correct Answer: D) Electrolytic cell

8. Zinc rod acts as anode in the Daniell cell but acts as cathode when coupled with aluminum electrode, this is because the standard reduction potential of:

A) Zn > Al

B) Zn < Al

C) Zn = Al

D) None of these

Correct Answer: A) Zn > Al

9. Electrolysis is a process in which the 'cations' and 'anions' liberated from electrolyte are:

A) hydrated

B) hydrolyzed

C) discharged

D) vaporized

Correct Answer: C) discharged

10. A cell which produces electric current by a redox reaction is called a/an:

A) Voltaic cell

B) Electrolytic cell

C) Half-cell

D) Standard cell

Correct Answer: A) Voltaic cell

11. The lead storage battery is a/an:

A) Down cell

B) Voltaic cell

C) Dry cell

D) Electrolytic cell

Correct Answer: B) Voltaic cell

12. The electrode potential of the standard hydrogen electrode is chosen as:

A) 0 V

Thermochemistry

Thermochemistry

Thermochemistry is dedicated to the quantitative study of thermal energy changes—specifically, heat transfers—that accompany chemical reactions and physical transformations. This field represents a direct application of the First Law of Thermodynamics to chemical processes, focusing on the energy inherently stored within substances, termed internal energy, and the energy exchanged with the surroundings as heat during reactions.

Fundamental principle

All chemical transformations involve the breaking of existing chemical bonds in the reactants, a process requiring an input of energy, and the formation of new bonds in the products, a process that releases energy. The net thermal effect observed—the heat of reaction—is the arithmetic difference between the total energy required for bond dissociation and the total energy liberated upon bond formation.

Heat

It is energy transferred due to temperature difference;

Temperature

It is average kinetic energy"

.**Energy Changes in Reactions:** During a chemical reaction, bonds in the reactants are broken (requiring energy) and new bonds in the products are formed (releasing energy). The net heat change of the reaction is the difference between these two energy values.

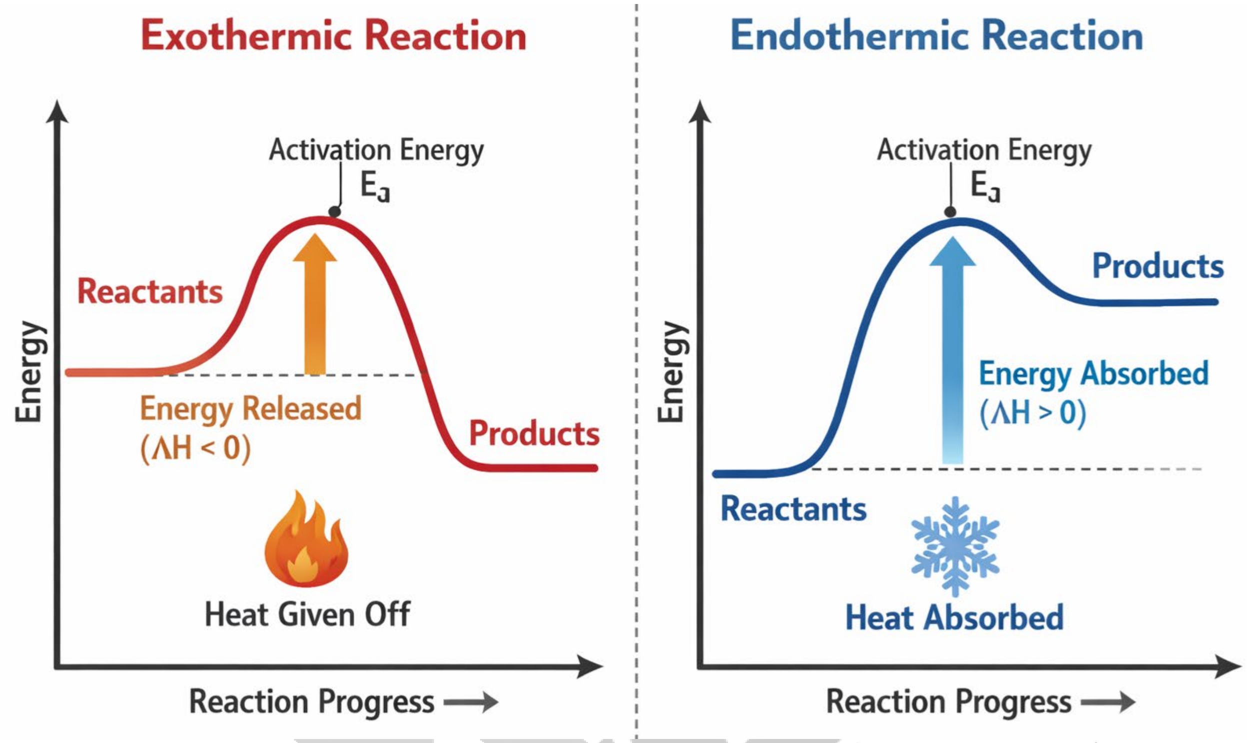
Sign Convention: The heat change of a reaction is denoted by **ΔH** (enthalpy change).

By convention:

ΔH = Negative (–ve): Exothermic Reaction. In such reactions, the system releases thermal energy to its surroundings. This is characteristic of processes like combustion, where the enthalpy of the products is lower than that of the reactants; the surplus energy manifests as heat, often accompanied by an increase in the temperature of the surroundings.

ΔH = Positive (+ve): Endothermic Reaction. Here, the system absorbs thermal energy from its surroundings. The enthalpy of the products is higher than that of the reactants, and the requisite energy is drawn from the environment, typically resulting in a cooling effect. A quintessential biological example is photosynthesis, where light energy is ultimately converted and stored as chemical energy within glucose molecules.

Photosynthesis: $6CO_2 + 6H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$; $\Delta H = +2800$ kJ/mol (endothermic)"



Key Thermodynamic Concepts

System, Surroundings, and Boundary

System: The specific part of the universe under study (e.g., reactants in a beaker).

Surroundings: Everything else in the universe outside the system.

Boundary: The real or imaginary surface that separates the system from the surroundings.

State and State Functions

The **state of a system** is its condition as described by a set of macroscopic, measurable properties such as temperature (T), pressure (P), volume (V), internal energy (E), and composition (e.g., number of moles, n). When these properties have definite, unchanging values, the system is said to be in a definite state.

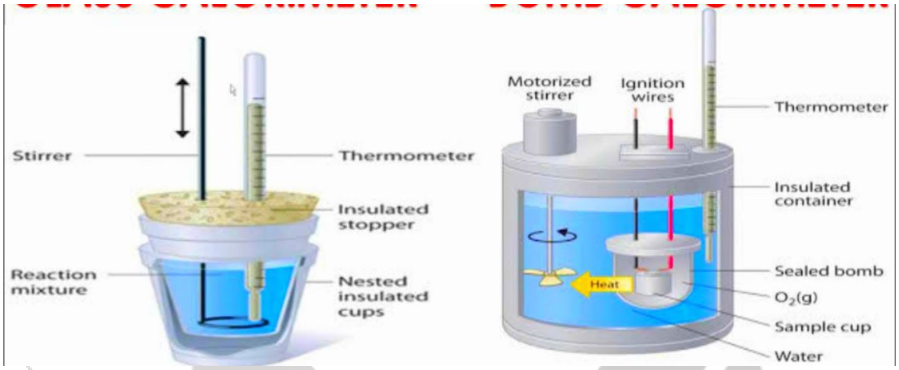
State function

(or state property) is a property whose value depends exclusively on the current, equilibrium state of the system, and not on the history or the specific path by which that state was achieved. The **change** in a state function (denoted by Δ, as in ΔV or ΔE) is determined solely by the values in the initial and final states **(Δ = Final State – Initial State).**

Common examples of state functions include **internal energy (E), enthalpy (H), pressure (P), volume (V), temperature (T), entropy (S), and Gibbs free energy (G).** These are path-independent.

In contrast, **heat (q)** and **work (w)** are **path functions**. Their magnitudes depend critically on the specific sequence of intermediate states traversed during a process. For instance, the work done in expanding a gas depends on whether the expansion occurs against a constant external pressure, reversibly, or in a series of steps; different paths yielding the same final volume will involve different amounts of work. Consequently, while we can discuss changes in state functions (ΔE, ΔH), it is incorrect to refer to "change the **change in internal energy (ΔE)** for the combustion reaction. To find the standard enthalpy of combustion (ΔH°c), one must then apply the correction ΔH = ΔE + Δn(g)RT.where **R = 8.314 J/mol·K = 0.0821 L·atm/mol·K = 1.987 cal/mol·K = 0.008314 kJ/mol·K**

At constant volume, **q_v = ΔE.(At constant volume, q_v = ΔE** only **if no non-PV work**)



Hess's Law of Constant Heat Summation

This is a fundamental law in thermochemistry, stated as:

The total enthalpy change for a reaction is the same, regardless of the number of steps in which the reaction is carried out, provided the initial and final conditions are the same.

In other words, enthalpy is a state function, so the pathway is irrelevant.

Applications:

Calculation of enthalpies of formation for compounds that cannot be synthesized directly from their elements (e.g., CO).

Determination of enthalpy changes for reactions that are slow or have side reactions.

Calculation of lattice energy and electron affinity via the Born-Haber cycle.

Methodology: Thermochemical equations can be treated algebraically—they can be added, subtracted, reversed (sign of ΔH changes), or multiplied by a coefficient (ΔH is multiplied by the same coefficient).

Example: Calculation of ΔH°*f* for CO (g)

Given:

1. C(graphite) + $O_2(g) \rightarrow CO_2(g)$ | $\Delta H_1 = -393.5$ kJ mol^{-1}
2. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ | $\Delta H_2 = -283.0$ kJ mol^{-1}

Target Equation: C (graphite) + ½ $O_2(g) \rightarrow CO(g)$ | ΔH_3 = ?

Subtracting equation (2) from equation (1) gives the target equation.

Therefore, $\Delta H_3 = \Delta H_1 - \Delta H_2 = (-393.5) - (-283.0) =$ **-110.5 kJ mol^{-1}**

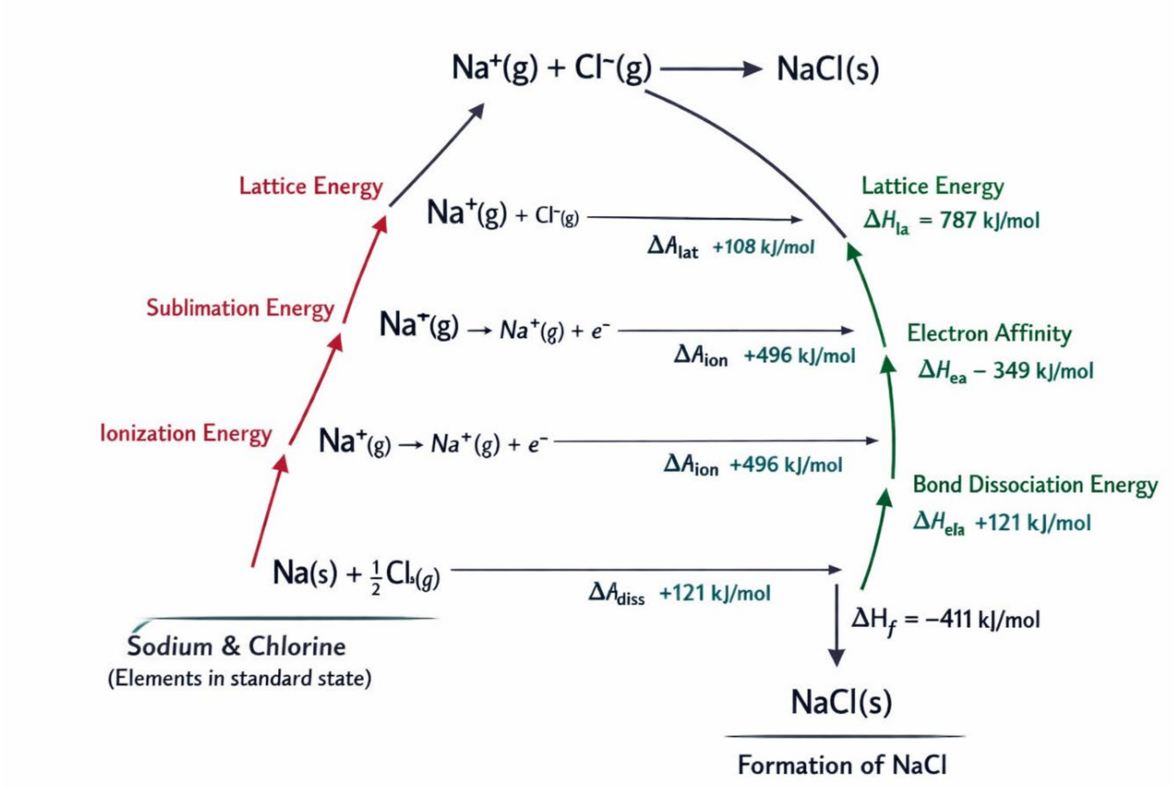
Remember (When reversing an equation, ΔH changes sign. When multiplying equation by n, multiply ΔH by n)

The Born-Haber Cycle

The Born-Haber cycle is a specific application of Hess's Law used to calculate the **Lattice Energy** of an ionic compound, which cannot be measured directly.

Lattice Energy (ΔH°_{latt}): The enthalpy change when one mole of an ionic crystal is formed from its constituent gaseous ions. It is a measure of the stability of the ionic lattice.

Cycle for NaCl: The cycle connects the standard enthalpy of formation of NaCl to other measurable quantities through a series of steps:

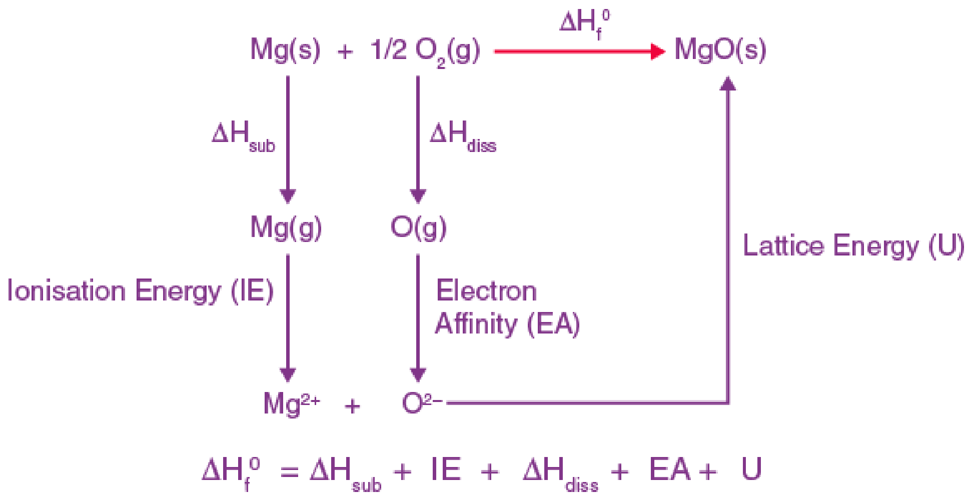


1. **Sublimation of Na(s):** Na(s) → Na(g) | $\Delta H^\circ_{su\beta}$
2. **Ionization of Na(g):** Na(g) → $Na^+(g) + e^-$ | ΔH°_i (Ionization Energy)
3. **Dissociation of Cl_2(g):** $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ | $\Delta H^\circ diss$ (Bond Energy)
4. **Electron Affinity of Cl(g):** $Cl(g) + e^- \rightarrow Cl^-(g)$ | ΔH°_{ea} (Electron Affinity)
5. **Lattice Formation:** $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ | ΔH°_{latt}

According to Hess's Law:

$$\Delta H^\circ f(NaCl) = \Delta H^\circ_{atm} + \Delta H^\circ_I + \tfrac{1}{2}\Delta H^\circ_{atm} + \Delta H^\circ_{Ea} + \Delta H^\circ_{latt}$$

This equation can be rearranged to calculate the unknown lattice energy.



Born Harber Cycle for Magnesium Oxide

A Born-Haber cycle for MgO, showing the stepwise path from elements to ionic solid and the direct path (ΔH°f). The sum of enthalpy changes around the cycle is zero.

Bond Energy

Bond Energy (or Bond Enthalpy) is the average energy required to break one mole of a particular type of bond in the gaseous state, separating the atoms.

It is a measure of bond strength.

Calculation of ΔH_r from Bond Energies:

$\Delta H_r = \Sigma$ (Bond Energies of Bonds Broken) – Σ (Bond Energies of Bonds Formed)

energy is absorbed to break bonds (+ve contribution).

Energy is released when bonds are formed (–ve contribution).

Variation of Enthalpy of Reaction with Temperature (Kirchhoff's Law)

The enthalpy change of a reaction depends on temperature. Kirchhoff's Law provides a way to calculate ΔH at one temperature if it is known at another.

$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$

Where:

- ΔH_2 and ΔH_1 are the enthalpy changes at temperatures T_2 and T_1, respectively.
- **$\Delta C_p = \Sigma C_p$ (products) – ΣC_p(reactants)**, the difference in the heat capacities at constant pressure.
- **Spontaneous and Non-Spontaneous Reactions**
- **Spontaneous Process:** A process that, once started, proceeds on its own without any external assistance (e.g., water flowing downhill, iron rusting).
- **Non-Spontaneous Process:** A process that does not occur on its own and requires a continuous external influence (e.g., pumping water uphill).

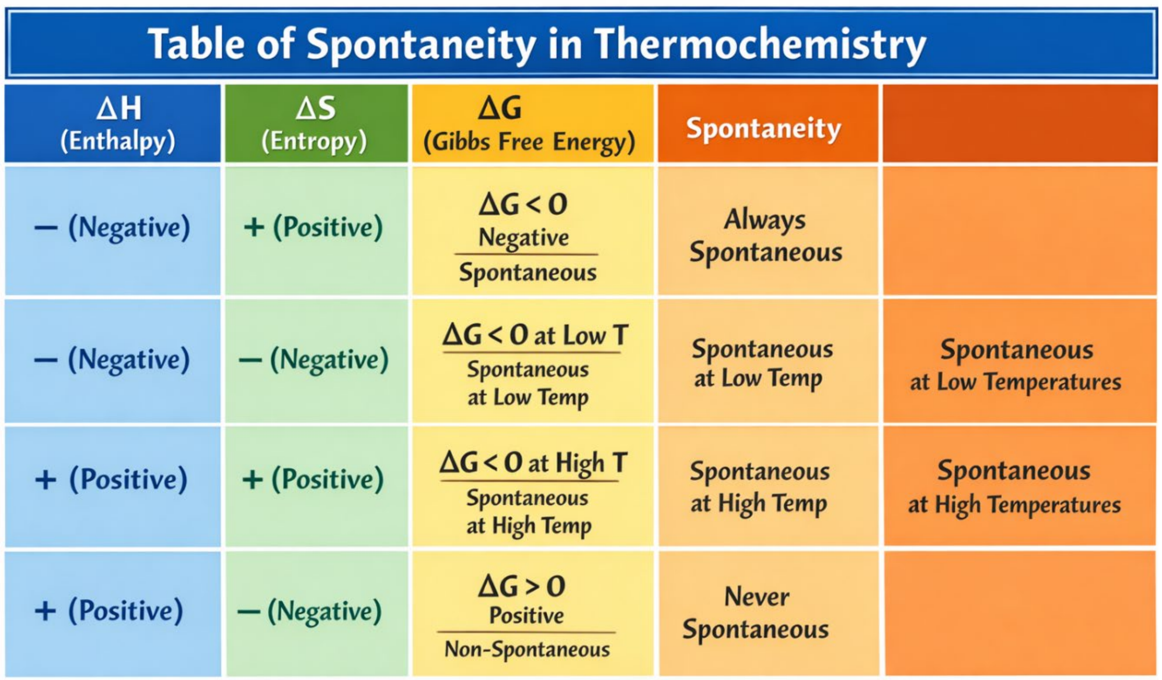


Table of Spontaneity in Thermochemistry

ΔH (Enthalpy)	ΔS (Entropy)	ΔG (Gibbs Free Energy)	Spontaneity	
– (Negative)	+ (Positive)	$\Delta G < 0$ Negative Spontaneous	Always Spontaneous	
– (Negative)	– (Negative)	$\Delta G < 0$ at Low T Spontaneous at Low Temp	Spontaneous at Low Temp	Spontaneous at Low Temperatures
+ (Positive)	+ (Positive)	$\Delta G < 0$ at High T Spontaneous at High Temp	Spontaneous at High Temp	Spontaneous at High Temperatures
+ (Positive)	– (Negative)	$\Delta G > 0$ Positive Non-Spontaneous	Never Spontaneous	

Important Note: While many spontaneous processes are exothermic, this is not always true. Endothermic processes can also be spontaneous (e.g., dissolving of NH_4Cl in water). Spontaneity is governed by both **enthalpy (ΔH)** and **entropy (ΔS)**, a measure of disorder, as described by the Gibbs free energy equation: $\boldsymbol{\Delta G = \Delta H - T\Delta S}$. A negative ΔG indicates a spontaneous process.

Topic-Wise One-Liners: Thermochemistry

Introduction to Thermochemistry

1. **Thermochemistry** is the study of heat energy changes accompanying chemical reactions and physical transformations.
2. An **exothermic** reaction releases heat to the surroundings, indicated by a **negative ΔH**.
3. An **endothermic** reaction absorbs heat from the surroundings, indicated by a **positive ΔH**.
4. **Energy** is defined as the capacity to do work.
5. The **Electron Volt (eV)** is the smaller unit of energy, used for sub-atomic particles.
6. The SI unit of energy is the **Joule (J)**.
7. One calorie is equal to **4.184 Joules**.
8. The bigger practical unit of energy is the **Kilowatt-hour (KWH)**, which equals 3.6 million Joules.

Systems and Surroundings

9. A **system** is the specific part of the universe under observation.
10. The **surroundings** comprise everything else in the universe outside the system.
11. The **boundary** is the real or imaginary surface separating the system from its surroundings.
12. An **open system** can exchange both matter and energy with its surroundings.
13. A **closed system** can exchange energy but not matter with its surroundings.
14. An **isolated system** can exchange neither matter nor energy with its surroundings.
15. The human body is an example of an **open system**.

State Functions and Path Functions

16. A **state function** is a property whose value depends only on the current state of the system, not the path taken to reach that state.
17. Examples of state functions are **Internal Energy (E), Enthalpy (H), Pressure (P), Volume (V), and Temperature (T)**.
18. **Heat (q)** and **Work (w)** are path functions, as their values depend on the path taken.
19. **Intensive properties** do not depend on the quantity of matter (e.g., Temperature, Density).
20. **Extensive properties** depend on the quantity of matter (e.g., Mass, Volume, Internal Energy).

First Law of Thermodynamics

21. The **First Law of Thermodynamics** states that energy cannot be created or destroyed, only converted from one form to another (Law of Conservation of Energy).
22. The mathematical expression of the first law is **$\Delta E = q + w$**, where ΔE is the change in internal energy, q is heat, and w is work.
23. The sign convention states that **heat absorbed by the system (q) is positive**, and **heat released by the system (q) is negative**.
24. The sign convention states that **work done on the system (w) is positive**, and **work done by the the system (w) is negative**.
25. For expansion against a constant external pressure, work is calculated as **$w = -P\Delta V$**.
26. A limitation of the first law is that it does not indicate the **direction** of a process.

Enthalpy (H)

27. **Enthalpy (H)** is a state function defined as **$H = E + PV$**.
28. The change in enthalpy (**ΔH**) is equal to the heat absorbed or released at **constant pressure (q_p)**.
29. For reactions involving gases, the relationship between ΔH and ΔE is **$\Delta H = \Delta E + \Delta nRT$**, where **Δn** is

Practice MCQs

1. Which of the following is always true for an exothermic reaction?

A) ΔH is positive

B) ΔH is negative

C) ΔS is positive

D) ΔG is negative

Answer: ΔH is negative

2. The branch of chemistry that deals with the energy changes in chemical reactions is called:

A) Electrochemistry

B) Thermochemistry

C) Chemical Kinetics

D) Stoichiometry

Answer: Thermochemistry

3. Which one of the following is an extensive property?

A) Temperature

B) Density

C) Internal Energy

D) Specific Heat

Answer: Internal Energy

4. In an isolated system, what can be exchanged with the surroundings?

A) Matter only

B) Energy only

C) Both matter and energy

D) Neither matter nor energy

Answer: Neither matter nor energy

5. A state function is:

A) Heat (q)

B) Work (w)

C) Enthalpy (H)

D) Both q and w

Answer: Enthalpy (H)

6. According to the first law of thermodynamics, the equation for the change in internal energy (ΔE) is:

A) $\Delta E = q - w$

B) $\Delta E = q / w$

C) $\Delta E = q + w$

D) $\Delta E = w - q$

Answer: $\Delta E = q + w$

7. For a system that absorbs heat and does work on the surroundings, the signs of q and w are respectively:

A) Negative, Negative

B) Positive, Positive

C) Positive, Negative

D) Negative, Positive

Answer: Positive, Negative

8. The work done by a system during an expansion against a constant external pressure is given by:

A) $w = P\Delta V$

B) $w = -P\Delta V$

C) $w = \Delta V/P$

D) $w = -\Delta V/P$

Answer: $w = -P\Delta V$

9. Enthalpy (H) is defined as:

A) $E - PV$

B) E / PV

C) $E + PV$

D) $PV - E$

Answer: $E + PV$

10. The heat change at constant pressure (q_p) is equal to:

A) ΔE

B) ΔH

C) ΔG

D) w

Answer: ΔH

11. For the reaction where the number of moles of gas decreases ($\Delta n < 0$), which relationship is correct?

A) $\Delta H = \Delta E$

B) $\Delta H > \Delta E$

C) $\Delta H < \Delta E$

D) $\Delta H = 0$

Answer: $\Delta H < \Delta E$

Chemical Equilibrium

IRREVERSIBLE REACTIONS

In an irreversible reaction, the process proceeds essentially to completion in one direction under a given set of conditions, with the reverse reaction being negligible. A classic example is the reaction of sodium with water:

$2Na(s) + 2H_2O(\ell) \rightarrow 2NaOH(aq) + H_2(g)$.

Under normal temperatures, the tendency for hydrogen gas to react with sodium hydroxide to reform sodium and water is so infinitesimally small that it is considered non-existent for practical purposes. Such reactions are said to be irreversible and are represented with a single arrow (→).

REVERSIBLE REACTIONS.

a reversible reaction is one in which the products can react to re-form the original reactants under the same conditions. Both forward and reverse processes occur simultaneously. A prime example is the reaction between nitrogen and hydrogen to form ammonia:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

When stoichiometric amounts of nitrogen and hydrogen are combined at 450°C under high pressure in the presence of an iron catalyst, the reaction mixture does not consist solely of ammonia after an indefinite time. Instead, it contains all three species—nitrogen, hydrogen, and ammonia—in fixed proportions, indicating that the reverse reaction (decomposition of ammonia) is occurring to a measurable extent. This state, where the composition of the mixture remains constant over time, is a hallmark of a reversible reaction, denoted by the double arrow symbol (⇌).

Examples of Reversible Reactions

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ (esterification)

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (thermal decomposition)

The **concept of reversibility is not absolute**

but depends on the conditions. For instance, the combustion of hydrogen to form water, $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$, appears **irreversible at room temperature** However, if water is heated to extremely high temperatures (around 1500°C), a noticeable quantity decomposes back into hydrogen and oxygen. This demonstrates that the reverse reaction does occur, but its rate is so slow at lower temperatures as to be imperceptible.

Chemical Equilibrium – Nature and Characteristics

When a reversible reaction is conducted in a closed system and allowed to proceed for a sufficiently long period without any change in external parameters such as temperature, pressure, or concentration, a point is reached where the macroscopic properties of the system become invariant with time. This condition is termed a state of chemical equilibrium. At equilibrium, the concentrations of all reactants and products remain constant. It is crucial to understand that this constancy is not due to the cessation of chemical activity but arises from a dynamic balance. The

- **Common ion effect** reduces ionization or solubility.
- **Salt hydrolysis** explains pH of salt solutions.
- **Indicators** are chosen based on pH range of the equivalence point.
- **Lewis theory** defines acids/bases by electron-pair acceptance/donation.

Topic Wise One-Liner: Chemical Equilibrium

1. Reversible Reactions

1. A **reversible reaction** proceeds in both forward and reverse directions simultaneously.
2. It is represented by a **double arrow (⇌)**.
3. Example: $H_2(g)+I_2(g)\rightleftharpoons 2HI(g)H_2(g)+I_2(g)\rightleftharpoons 2HI(g)$.
4. Esterification and thermal decomposition of calcium carbonate are examples of reversible reactions.
5. An **irreversible reaction** goes nearly to completion in one direction under normal conditions.
6. Example of irreversible reaction: $2Na+2H_2O\rightarrow 2NaOH+H_2$

2. Chemical Equilibrium – Nature and Characteristics

7. Chemical equilibrium is **dynamic**, not static.

8. At equilibrium, **forward and reverse reaction rates are equal**.

9. Concentrations of reactants and products remain **constant** at equilibrium.

10. Equilibrium can be reached starting from **pure reactants or pure products**.

11. Equilibrium is attainable only in a **closed system**.

12. A **catalyst** speeds up both forward and reverse reactions equally but does **not shift equilibrium position**.

13. The **equilibrium constant (K)** depends only on **temperature**, not on initial concentrations.

14. At equilibrium, **$\Delta G = 0$** and the system is at minimum free energy.

3. Law of Mass Action

15. The **Law of Mass Action** states that the rate of a reaction is proportional to the product of molar concentrations of reactants raised to their stoichiometric coefficients.

16. For $aA+bB\rightarrow aA+bB\rightarrow$ products, rate $=k[A]a[B]b=k[A]a[B]b$.

17. For a reversible reaction $aA+bB\rightleftharpoons cC+Dd$ at equilibrium $kf\,[A]a[B]b=kr\,[C]c[D]d$

18. The **equilibrium constant Kc** is derived as $Kc=kf/kr=[C]c[D]d/[A]a[B]b$

4. Equilibrium Constant (Kc)

19. **Kc** is expressed in terms of molar concentrations.

20. For reactions involving gases, the equilibrium constant can be expressed in terms of partial pressures and is denoted as **Kp**. Pure solids and liquids are omitted.

21. Pure solids and liquids are **omitted** from the equilibrium expression.

22. Example: For $N2+3H_2\rightleftharpoons 2NH_3$, $Kc=[NH_3]^2/[N_2][H_2]^3$

23. $Kp=Kc(RT)^{\Delta n}$ where Δn=(moles of gaseous products)−(moles of gaseous reactantants)

24. If $\Delta n=0$ then $Kp=Kc$

25. Units of **Kc** are $(mol\ L-1)\Delta^n$ and of **Kp** are $(atm)^{\Delta n}$

87. **Hydrolysis constant Kh** for anion hydrolysis: $Kh=Kw/Ka$.

88. For cation hydrolysis: $Kh=Kw/Kb$

15. Acid–Base Titrations and Indicators

89. **Titration** is a volumetric method to determine unknown concentration using a standard solution.

90. Strong acid–strong base titration uses **phenolphthalein** (pH 8.2–10.0) as indicator.

91. Strong acid–weak base titration uses **methyl orange** (pH 3.1–4.4).

92. Weak acid–strong base titration uses **phenolphthalein**.

93. Weak acid–weak base titration has **no sharp end point**.

94. Titration formula: $M1V1/n1=M2V2/n2$

16. Lewis Acids and Bases

95. **Lewis acid** is an electron-pair acceptor (e.g., BF_3, H^+).

96. **Lewis base** is an electron-pair donor (e.g., NH_3, OH^-).

97. Example: $BF_3+:NH_3 \rightarrow F_3B:NH_3$

Practice MCQs

1. The symbol used to represent a reversible reaction is:

A) →

B) ←

C) ⇒

D) ⇌

Answer: **⇌**

2. An example of a reversible reaction is:

A) $2Na + 2H_2O \rightarrow 2NaOH + H_2$

B) $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

C) $H_2 + I_2 \rightleftharpoons 2HI$

D) $2H_2 + O_2 \rightarrow 2H_2O$

Answer: **$H_2 + I_2 \rightleftharpoons 2HI$**

3. At dynamic equilibrium, the rates of the forward and reverse reactions are:

A) Zero

B) Increasing

C) Decreasing

D) Equal

Answer: **Equal**

4. Chemical equilibrium can only be established in a:

A) Open system

B) Closed system

C) Isolated system

D) Any system

Answer: **Closed system**

5. A catalyst affects a system at equilibrium by:

A) Shifting the equilibrium position

B) Changing the equilibrium constant

C) Increasing the rate at which equilibrium is attained

D) Decreasing the activation energy of the reverse reaction only

Answer: **Increasing the rate at which equilibrium is attained**

6. The equilibrium constant (K) for a reaction depends only on:

A) Pressure

B) Concentration

C) Temperature

D) Catalyst

Answer: **Temperature**

7. According to the Law of Mass Action, the rate of a reaction is proportional to the:

A) Sum of the concentrations of reactants

B) Product of the concentrations of reactants raised to their stoichiometric coefficients

C) Difference in concentrations of products and reactants

Solved Past Papers MCQs

1. Empirical formula and molecular formula of a compound
A) are always same
B) are always different
C) may be same or different
D) are same only for inorganic compounds
Answer: (C)

2. 250 mL of a 0.50 M NaOH solution is diluted with water to a volume of 500 mL. The concentration of new solution is
A) 0.025 M
B) 0.050 M
C) 0.250 M
D) 0.125 M
Answer: (D)

3. Which of the following is primary standard for use in standardizing bases?
A) Potassium hydrogen phthalate
B) Ammonium hydroxide
C) Silver nitrate
D) Acetic acid
Answer: (A)

4. In chromatography, which of the following can the mobile phase be made of?
A) Liquid only
B) Gas only
C) Liquid or gas
D) Solid or liquid
Answer: (C)

5. Octane number of any fuel can be improved by _____ process.
A) pyrolysis
B) polymerization
C) condensation
D) reforming
Answer: (D)

6. With increase in temperature, the concentration of a solution expressed in molarity generally _____.
A) increases
B) decreases
C) varies randomly
D) unchanged
Answer: (B)

7. The following stereoisomers are related as
A) Epimers
B) Enantiomers
C) Diastereomers
D) They are identical stereoisomers
Answer: (B)

8. The sea level will be _____ due to global warming.
A) increased
B) decreased
C) depreciated
D) unaffected
Answer: (A)

9. Which of the followings is the strongest acid?
A) $ClCH_2COOH$
B) $BrCH_2COOH$
C) ICH_2COOH
D) FCH_2COOH
Answer: (D)

10. Which one of the following acids is a basic amino acid?
A) Glycine
B) Lysine
C) Alanine
D) Glutamic acid
Answer: (B)

11. The ground-state atom of which of the following transition metals contains an unpaired electron in the s-orbital?
A) Iron
B) Nickel
C) Chromium
D) Cobalt
Answer: (C)

12. What is the oxidation state of Xe in Ba_2XeO_6?
A) 4
B) 6
C) 8
D) 10
Answer: (C)

13. Nuclear fission reaction of ^{235}U needs _____ neutrons.
A) medium energy

B) thermal
C) slow
D) fast
Answer: (B)

14. Which of the following transitions is the highest energy transition?
A) $n \rightarrow \sigma^*$
B) $\sigma \rightarrow \sigma^*$
C) $n \rightarrow \pi^*$
D) $\pi \rightarrow \pi^*$
Answer: (B)

15. The self-linking property of carbon is called
A) hybridization
B) cracking
C) isomerism
D) catenation
Answer: (D)

16. Which of the following ion is kinetically inert?
A) Ti^{3+}
B) Cr^{3+}
C) Rh^{3+}
D) Ru^{2+}
Answer: (C)

17. Which is not the characteristic of a primary standard?
A) stability
B) high purity
C) low molar mass
D) non-hygroscopic
Answer: (C)

18. Which of the following is Van't Hoff's equation for dilute solutions?
A) $p = Vn/RT$
B) $p = VnR/T$
C) $pV = n/RT$
D) $\pi V = nRT$
Answer: (D)

19. A reaction between reactants 'A and B' is second order. The rate law which might possibly apply to the reaction is
A) Rate = k[A][B]
B) Rate = k[A]2
C) Rate = k[B]2
D) All are equally possible
Answer: (D)

20. Coal is believed to be produced after a long-time decay of
A) ores
B) wood
C) animals
D) fossils
Answer: (B)

21. Which one of the following is not a colligative property?
A) Osmotic pressure
B) Depression in freezing point
C) Freezing point
D) Elevation in boiling point
Answer: (C)

22. Which of the following cracking process requires the lowest temperature?
A) Catalytic cracking
B) Thermal cracking
C) Steam cracking
D) Cracking is independent of temperature
Answer: (A)

23. Lock and key mechanism is observed in _____ chromatography.
A) size exclusion
B) affinity
C) ion exchange
D) reverse phase
Answer: (B)

24. The empirical determination of the relationship between the quantity measured in an analysis and the analyte concentration is
A) titration
B) standardization
C) calibration
D) quantification
Answer: (C)

25. Which of the following fractions of petroleum has the highest boiling point range?
A) Gasoline
B) Kerosene
C) Petroleum ether
D) Liquid
Answer: (B)

86. Heating of rubber with sulphur is known as
A) Galvanization
B) Vulcanization
C) Bessemerization
D) Sulphonation
Answer: (B)

87. The following conversion can be accomplished with which of the following reagent?
A) $LiAlH_4$
B) HCl, H_2O, heat
C) H_2NNH_2, heat
D) $NaOH$, H_2O, heat
Answer: (B)

88. Which of the following product is prepared by the dry distillation of calcium acetate?
A) Formic acid
B) Acetic acid
C) Acetone
D) All of the above
Answer: (C)

89. For the quadratic equation $5x^2 - 3x - 1 = 0$ the solution set is
A) 1, 1/3
B) $(3 \pm 29)/10$
C) $(3 \pm \sqrt{29})/10$
D) $(3 \pm \sqrt{11})/10$
Answer: (C)

90. Correct IUPAC name of the compound shown below is _____.
A) 3-Ethyl-4-methylheptane
B) 3-Ethyl-4,7-dimethylnonane
C) 3-Methyl-7-ethyldecane
D) 3,4-Diethyl-5,7-dimethylnonane
Answer: (B)

91. Which of the following ketones will produce propanoic acid only after oxidation by acidified potassium dichromate?
A) Diethyl ketone
B) Dimethyl ketone
C) Ethyl methyl ketone
D) Ethyl n-propyl ketone
Answer: (A)

92. Which of the following compounds does not undergo Cannizzaro's reaction?
A) Acetone
B) Methanol
C) Benzaldehyde
D) Trimethyl acetaldehyde
Answer: (A)

93. For a reaction A + B → products, it is observed that doubling the concentration of A causes the reaction rate to become two times while doubling the concentration of B does not affect the rate. The reaction rate can be expressed as ______.
A) $k[A][B]$
B) $k[A]^2$
C) $k[A]$
D) $k[A]^2[B]^2$
Answer: (C)

94. The configuration for the carbon marked with asterisk sign (*) in the formula shown is ______.
A) R
B) L
C) S
D) D
Answer: (C)

95. The magnitude of the vector $1i + 2j + 3k$ is ______.
A) 6
B) 14
C) $\sqrt{14}$
D) $(14)^2$
Answer: (C)

96. An S_N1 reaction results in ______.
A) Retention
B) Elimination
C) Inversion
D) Racemisation
Answer: (D)

97. Of the following compounds, which of the following reacts most rapidly with water?
A) CH_3CONH_2
B) $CH_3COOCOCH_3$
C) CH_3COCl
D) CH_3COOCH_3
Answer: (C)

394. How many significant figures are there in 00.4793?
A) 3
B) 4
C) 5
D) 6
Answer: (B)

395. Which one of the following is NOT a meta directing group?
A) COOH
B) SO3H
C) CHO
D) OH
Answer: (D)

396. The rate of a chemical reaction is directly proportional to the product of active masses of the reactants, it is referred to as:
A) Law of conservation of energy
B) Law of mass action
C) Law of conservation of mass
D) Active mass law
Answer: (B)

397. Which one of the following does NOT give iodoform test?
A) CH3OH
B) CH3CH2OH
C) CH3CHO
D) CH3COCH3
Answer: (A)

398. The boiling point of water is highest than other hydrides because water molecules can form:
A) 4 hydrogen bonds
B) 3 hydrogen bonds
C) 2 hydrogen bonds
D) 1 hydrogen bond
Answer: (A)

399. The reaction 2CO + O2 → 2CO2 proceeds slower because of activation energy of CO.
A) Equilibrium
B) Constant
C) Low
D) High
Answer: (D)

400. Lithium and beryllium are unique in such a way that they have higher charge densities which produce strong polarizing effects due to:
A) Solubility
B) Small size
C) Large size
Answer: (B)

401. The Neutron was discovered by:
A) Goldstein
B) Rutherford
C) JJ Thomson
D) Chadwick
Answer: (D)

402. The normal pH of blood is:
A) 7.75
B) 7.35
C) 7.25
Answer: (B)

403. Which of the following reactions is NOT shown by Ketones?
A) Reaction with HCN
B) Reaction with Fehling solution
C) Reaction with NaHSO3
D) Reaction with 2,4-dinitrophenylhydrazine
Answer: (B)

404. The melting point of NaCl is very high 801°C. It is reduced to 600°C by addition of ___ in Down's process.
A) Calcium chloride
B) Magnesium chloride
C) Aluminum chloride
D) Potassium chloride
Answer: (A)

405. The phenomenon in which certain elements emit invisible radiations is called:
A) Spectroscopy
B) Radioactivity
C) Gravimetry
D) Chromatography
Answer: (B)

406. The number of bond(s) between carbon and nitrogen atoms in Nitriles is:
A) One sigma and one pi
B) Two sigma and one pi
C) Only sigma
D) One sigma and two pi
Answer: (D)