

FSc Part-I (1st Year) · PECTAA Board · English Medium

Chemistry 1st Year

Complete Notes — All 16 Chapters

freebooks.pk



Table of Contents

Chapter 1	Periodic Table and Periodic Properties
Chapter 2	Atomic Structure
Chapter 3	Chemical Bonding
Chapter 4	Stoichiometry
Chapter 5	States and Phases of Matter
Chapter 6	Chemical Energetics
Chapter 7	Reaction Kinetics
Chapter 8	Chemical Equilibrium
Chapter 9	Acid-Base Chemistry
Chapter 10	Electrochemistry
Chapter 11	Hydrocarbons
Chapter 12	Nitrogen and Sulfur
Chapter 13	Halogens
Chapter 14	Atmosphere
Chapter 15	Basic Separation Techniques
Chapter 16	Lab Safety and Practical Skills

Prepared by freebooks.pk — original student notes covering the Updated/Revised National Curriculum of Pakistan 2023, PECTAA Board syllabus. Each chapter includes key concepts, definitions, formulas, diagrams, short and long questions, MCQs, revision and exam tips.

© Freebooks.pk — **DMCA-protected**. These notes are copyrighted and may be shared or linked **without any changes**. Original educational content created by the Freebooks.pk Editorial Team.
Internal Reference: **FBPK-CHEM11-2026-08**



Chapter 1: Periodic Table and Periodic Properties

The periodic table is often called the 'symbol of chemistry' -- a single chart that organizes all 118 known elements by atomic number and, in doing so, predicts and explains an enormous range of chemical behaviour. This chapter traces how that organization was built, from early 19th-century attempts to group elements by similarity through to Mendeleev's landmark mass-based table and Moseley's decisive shift to atomic number, and then examines the modern table's structure: its periods, groups, blocks, and the six families of elements that share closely related properties.

The second half of the chapter turns to periodicity itself -- the systematic way atomic radius, ionic radius, ionization energy, electron affinity, electronegativity, and metallic character all rise or fall in predictable patterns across periods and down groups. These trends are then applied directly to the chemistry of Period 3: the contrasting reactions of sodium and magnesium with water, oxygen, and chlorine, and the shift from ionic, basic oxides and neutral chlorides at the metal end of the period to covalent, acidic oxides and hydrolysing chlorides at the nonmetal end.

Learning Objectives

- Explain the arrangement of elements in the periodic table and identify the positions of metals, nonmetals, and metalloids
- Explain that the periodic table is arranged into four blocks (s, p, d, f) associated with the four subshells
- Deduce an element's electron configuration from its position in the periodic table, and vice versa
- State that the principal energy level and number of valence electrons can be deduced from an element's position in the table
- Predict the characteristic properties of an element in a given group using knowledge of chemical periodicity



- Explain the vertical and horizontal trends in atomic radius, ionic radius, ionization energy, electron affinity, and electronegativity
- Recognize that trends in metallic and nonmetallic behaviour arise from trends in valence electrons
- Suggest the type of chemical bonding present in oxides and chlorides from their physical and chemical properties
- Describe, with equations, the reactions of oxides and chlorides with water, including the likely pH of the resulting solutions
- Write equations for the reactions of sodium and magnesium with oxygen, chlorine, and water, and explain the variation in oxidation number of their oxides and chlorides

Key Concepts

1.1 Historical Background of the Periodic Table

Early classification attempts began with Lavoisier separating known elements into metals and nonmetals, followed by Dobereiner's Law of Triads (1829), which grouped elements such as lithium, sodium and potassium where the middle element's atomic weight was roughly the average of the other two. Newlands' Law of Octaves (1864) arranged the 62 elements then known by increasing atomic mass and noticed that every eighth element resembled the first, while in the same year Lothar Meyer plotted atomic volume against atomic weight and found a similar periodicity.

Mendeleev's 1869 table, arranging 63 elements by increasing atomic mass, succeeded where earlier attempts fell short because he deliberately left gaps for undiscovered elements and predicted their properties -- predictions later confirmed by discovery. This success established him as the father of the periodic table, though mass-based ordering still produced a handful of inconsistencies. In 1913, Moseley used X-ray emission data to determine each element's true atomic number, resolving these anomalies and reformulating the Periodic Law: the properties of elements are periodic functions of their atomic number, not atomic mass -- the version used today.



1.2 Structure of the Modern Periodic Table

The modern periodic table arranges 118 known elements in order of increasing atomic number across seven horizontal periods and eighteen vertical groups. Elements in the same group share the same number of valence electrons and therefore similar chemical behaviour, while physical properties change gradually down a group; elements across a period show a steady left-to-right change in properties as electrons fill the same outer shell.

Elements are also classified as metals (which lose electrons to form positive ions, occupying the left and centre of the table), nonmetals (which gain electrons to form negative ions, occupying the upper right), and metalloids (elements straddling the zig-zag 'stair-step' line running from boron down to polonium, showing mixed metallic and nonmetallic behaviour). A second classification divides the table into four blocks -- s, p, d and f -- named for the subshell holding the atom's last-added valence electron: Groups 1-2 form the s-block, Groups 13-18 the p-block, the transition elements the d-block, and the lanthanides and actinides beneath the main table the f-block.

1.3 Element Families

Six families of elements share closely related properties. Alkali metals (Group 1: Li, Na, K, Rb, Cs, Fr) have a single valence electron and are the most reactive metals, forming alkalis in water. Alkaline earth metals (Group 2: Be, Mg, Ca, Sr, Ba, Ra) have two valence electrons and are less reactive than alkali metals. Transition metals occupy the d-block, plus the f-block lanthanides and actinides below the main table, show variable oxidation states, and typically form coloured compounds.

Chalcogens (Group 16: O, S, Se, Te, Po, Lv) range from nonmetals (O, S) through metalloids (Se, Te, Po) to a metal (Lv). Halogens (Group 17: F, Cl, Br, I, At, Ts) are highly reactive nonmetals with strong electron affinities that readily accept one electron to complete their outer shell, forming salts with metals -- the origin of the name 'halogen', meaning salt-former. Noble gases (Group 18) have completely filled outer shells and are almost entirely unreactive, though a small number of noble-gas compounds, such as xenon hexafluoroplatinate, do exist.



1.4 Periodic Arrangement and Electron Configuration

An element's position in the periodic table directly encodes its electron configuration. The period number equals the highest occupied shell number (n), while the group number indicates the number of valence electrons -- for a main-group element, its block identifies which subshell those valence electrons occupy. For example, an element in period 3, group 2 has two electron shells filled plus a third shell containing two valence electrons in the 3s subshell (s-block), identifying it as magnesium.

This relationship works in both directions: given an element's group and period, its full or valence electron configuration can be deduced without consulting a table, and conversely, an element's group and period can be identified from a given configuration. This deduction is central to predicting chemical behaviour, since valence electron count and arrangement determine how readily an atom loses, gains, or shares electrons.

1.5 Atomic Radius, Ionic Radius, and Ionization Energy

Atomic radius, half the distance between two identical bonded atoms, depends on the number of electron shells, effective nuclear charge, and the shielding effect of inner electrons. It decreases across a period, since increasing nuclear charge pulls the electron cloud inward, and increases down a group, since additional shells outweigh the increased nuclear charge. Ionic radius follows a related but distinct pattern: cations are smaller than their parent atom, having lost an entire outer shell, anions are larger, since added electrons increase inter-electron repulsion and expand the electron cloud, and both cations and anions increase in size down a group.

Ionization energy is the energy needed to remove an electron from a gaseous atom or ion; each successive ionization energy for the same element is larger than the last, since removing an electron from an increasingly positive ion requires more energy. It is governed by nuclear charge, atomic or ionic size, and electron arrangement -- half-filled and fully-filled subshells are extra stable, giving elements like nitrogen or beryllium anomalously high first ionization energies compared with their immediate neighbours oxygen or boron. Ionization energy increases across a period, peaking at the noble gases with their stable



filled shells and reaching a minimum at the alkali metals, and decreases down a group as atomic size and shielding both increase.

1.6 Electron Affinity, Electronegativity, and Metallic Character

Electron affinity is the energy change when an electron is added to a gaseous atom; first electron affinities are usually negative, meaning energy is released, because the nucleus attracts the incoming electron, while second electron affinities are positive, since energy must be supplied to overcome repulsion from the existing negative charge. Electron affinity becomes more negative across a period, reflecting smaller atoms and higher nuclear charge, and less negative down a group, as larger atoms weaken the attraction, though half-filled subshells such as those in nitrogen and phosphorus give unexpectedly low values.

Electronegativity measures an atom's power to attract a shared pair of electrons in a bond, and on the Pauling scale it rises from about 0.8 for alkali metals to 4.0 for fluorine. It increases across a period, driven by rising nuclear charge and shrinking size, and decreases down a group, as added shells and shielding weaken the pull on bonding electrons. Metallic character -- the tendency to lose electrons -- follows the reverse of electronegativity: it decreases across a period as atoms hold their valence electrons more tightly, and increases down a group as atomic size and shielding make electron loss easier, explaining why caesium is far more reactive than sodium or lithium.

1.7 Reactions of Sodium and Magnesium

Sodium reacts vigorously with cold water to form sodium hydroxide and hydrogen gas, while magnesium reacts only slowly with cold water but much more vigorously with steam, forming magnesium oxide and hydrogen instead. Both metals burn in oxygen: sodium forms a mixture of sodium oxide and sodium peroxide with a golden-yellow flame, and is stored under kerosene to prevent this reaction occurring in air, while magnesium burns with an intense white flame to form magnesium oxide -- a reaction vigorous enough to be used in flares and fireworks.

Both metals also react directly and exothermically with chlorine gas to form their respective chlorides: sodium chloride and magnesium chloride, both white ionic solids. Across all three reactions, sodium is consistently the more reactive of the



two metals, consistent with alkali metals being more reactive than alkaline earth metals of the same period.

1.8 Bonding and Acid-Base Trends in Period 3 Oxides and Chlorides

Moving across period 3, the oxides change character from strongly ionic (Na_2O , MgO -- giant ionic lattices) to increasingly covalent (SO_2 , SO_3 , P_2O_5 -- discrete covalent molecules), a shift driven by increasing electronegativity and decreasing ionic character. Oxides are classified by their reaction with water: basic oxides, formed by metals such as Na_2O and CaO , produce alkaline solutions; acidic oxides, formed by nonmetals such as SO_2 and P_2O_5 , produce acidic solutions; and amphoteric oxides, such as Al_2O_3 , react with both acids and bases, forming a salt and water in each case.

Chlorides show a parallel pattern: NaCl and MgCl_2 dissolve in water to give solutions close to neutral, a simple hydration of ions, while AlCl_3 and the chlorides of silicon and phosphorus undergo hydrolysis, reacting with water to release HCl and produce acidic solutions. The oxidation number of a period 3 element in its oxide or chloride matches its group number, since oxygen and chlorine are more electronegative and the element itself is always assigned the positive oxidation state, rising from +1 in sodium to +6 in sulfur's oxide; elements such as phosphorus and sulfur show variable oxidation numbers because they can expand their octet using empty 3d orbitals.

Important Definitions

What is the Modern Periodic Law?

The physical and chemical properties of elements are periodic functions of their atomic numbers -- established by Moseley in 1913 using X-ray emission data.

What is atomic radius?

Half the distance between the nuclei of two identical atoms bonded together, typically measured in picometers (pm) or angstroms ($\text{\AA}$).

What is ionic radius?

The distance from the nucleus of an ion to its outermost electron shell in a crystal lattice; cations are smaller and anions are larger than their parent atoms.



What is first ionization energy?

The energy needed to remove one electron from each atom in one mole of gaseous atoms of an element, forming one mole of gaseous 1+ ions.

What is first electron affinity?

The enthalpy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous uni-negative ions.

What is electronegativity?

The power of an atom to attract a shared pair of electrons toward itself within a covalent bond, measured on the dimensionless Pauling scale.

What is metallic character?

An element's tendency to lose electrons and form positive ions; it decreases across a period and increases down a group.

What is a basic oxide?

An oxide, usually formed by a metal, that reacts with water to produce an alkaline (basic) solution, such as Na₂O or CaO.

What is an acidic oxide?

An oxide, usually formed by a nonmetal and held together by covalent bonds, that reacts with water to produce an acidic solution, such as SO₂ or P₂O₅.

What is an amphoteric oxide?

An oxide that can react with both acids and bases, behaving as either depending on conditions -- aluminium oxide (Al₂O₃) is the standard example.

Key Facts and Relations

Topic	Key Fact / Relation
General first ionization energy	$M(g) \rightarrow M^{+}(g) + e^{-}$, always endothermic (energy absorbed)
Sodium, 1st ionization energy	$Na(g) \rightarrow Na^{+}(g) + e^{-}$, $\Delta H_{i1} = +494 \text{ kJ/mol}$
Calcium, 2nd ionization energy	$Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-}$, $\Delta H_{i2} = +1150 \text{ kJ/mol}$
Chlorine, 1st electron affinity	

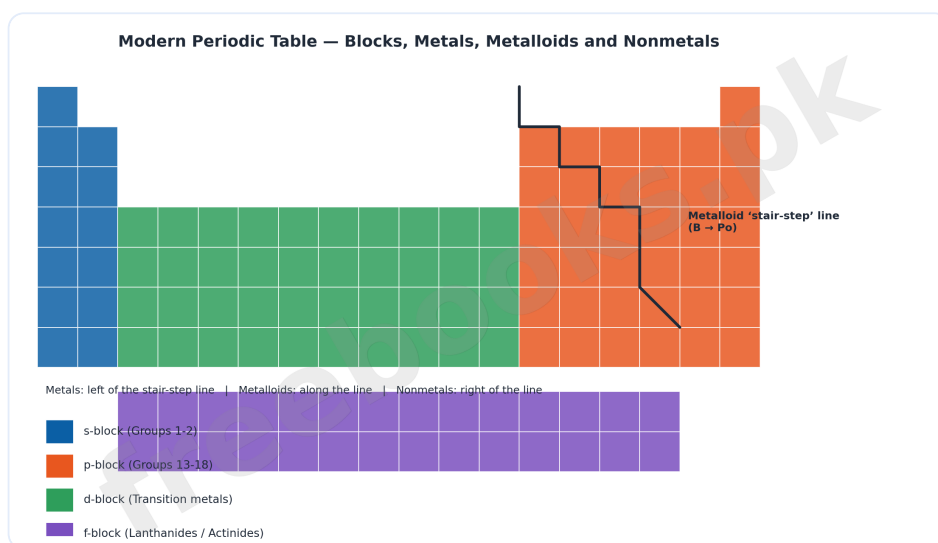


Topic	Key Fact / Relation
	$\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g}), \Delta H^\circ_{\text{ea1}} = -348.8 \text{ kJ/mol}$ (energy released)
Oxygen, 2nd electron affinity	$\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g}), \Delta H^\circ_{\text{ea2}} = +798 \text{ kJ/mol}$ (energy absorbed, due to repulsion)
Electronegativity range (Pauling scale)	Alkali metals lowest (about 0.8) up to fluorine highest (4.0)
Sodium with water	$2\text{Na(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)} + \text{H}_2(\text{g})$
Magnesium with steam	$\text{Mg(s)} + 2\text{H}_2\text{O(g)} \rightarrow \text{MgO(s)} + 2\text{H}_2(\text{g})$
Basic oxide with water	$\text{Na}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)}$
Amphoteric oxide with acid and base	$\text{Al}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$; $\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$

Diagrams

Periodic Table Blocks and the Metal-Metalloid-Nonmetal Divide: A

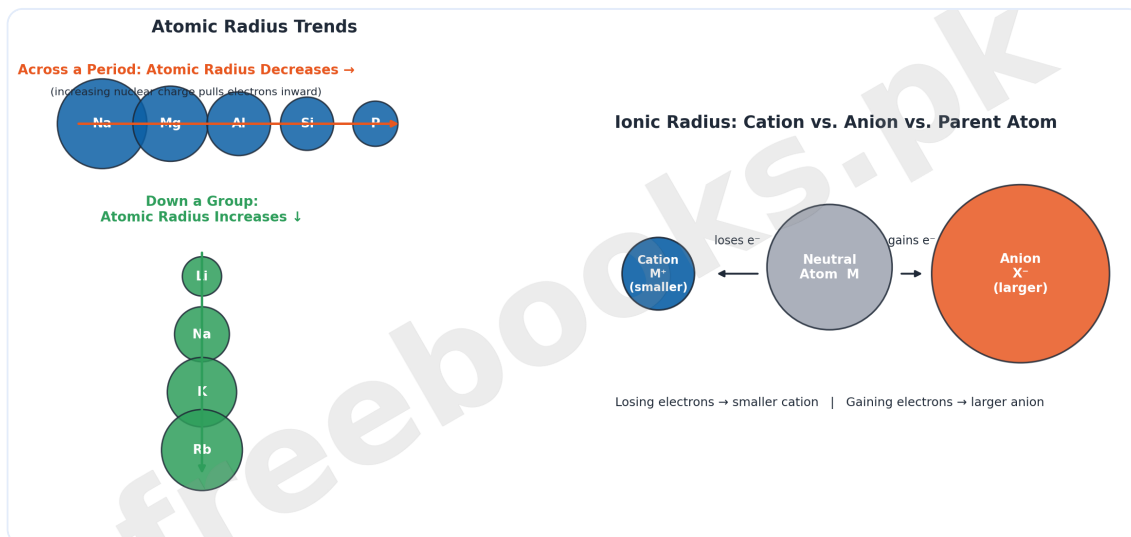
schematic periodic table grid showing the s-block, p-block, d-block and f-block regions in different colours, together with the zig-zag stair-step line running from boron to polonium that separates metals from nonmetals, with metalloids straddling the line



Periodic Table Blocks and the Metal-Metalloid-Nonmetal Divide

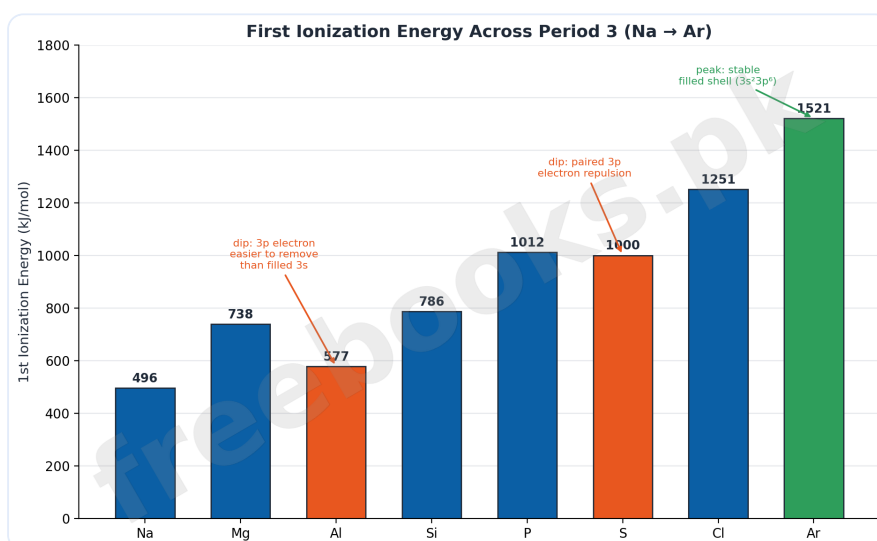


Atomic Radius and Ionic Radius Trends: Two panels comparing atom sizes: the left panel shows atomic radius shrinking across a period and growing down a group; the right panel compares a neutral atom with its cation, which is smaller, and its anion, which is larger



Atomic Radius and Ionic Radius Trends

First Ionization Energy Across Period 3: A bar chart of the first ionization energies of the Period 3 elements from sodium to argon, showing the overall increasing trend from left to right with a dip at aluminium and at sulfur due to subshell stability, and a peak at argon



First Ionization Energy Across Period 3



Short Questions & Answers

Which scientist first observed periodicity among the elements, and how?

English chemist John Newlands, in 1864, arranged the then-known 62 elements in increasing order of atomic mass and noticed that every eighth element resembled the first -- an early form of periodicity later named the Law of Octaves.

Why did Moseley's atomic-number-based arrangement succeed where Mendeleev's mass-based table had inconsistencies?

Moseley used X-ray emission data to determine each element's true atomic number, showing that atomic number, not atomic mass, is the property periodic law depends on, resolving several ordering anomalies in Mendeleev's table.

Why are Group 1 and Group 2 elements called s-block elements?

Because their valence, outermost electrons occupy the s subshell of their highest energy shell -- one electron in Group 1, two in Group 2.

Why is sulfur's first ionization energy lower than phosphorus's, even though sulfur has a higher nuclear charge?

Phosphorus has a stable, half-filled $3p^3$ subshell that resists losing an electron; sulfur's $3p^4$ configuration has one paired electron, and the extra repulsion between the paired electrons makes that electron easier to remove, lowering sulfur's ionization energy below phosphorus's despite sulfur's greater nuclear charge.

Why does aluminium chloride form an acidic solution in water while sodium chloride does not?

$AlCl_3$ is small and highly charged, so its Al^{3+} ion polarises water molecules strongly and undergoes hydrolysis, releasing H^+ ions and lowering the pH; $NaCl$ simply dissociates into hydrated Na^+ and Cl^- ions without reacting further, leaving the solution neutral.

What determines whether an oxide of a period 3 element is basic, acidic, or amphoteric?

Basic oxides are formed by metals on the left of the period, such as Na_2O and MgO , and react with water to form alkalis; acidic oxides are formed by nonmetals



on the right, such as P_2O_5 and SO_3 , and react with water to form acids; amphoteric oxides such as Al_2O_3 , near the metal-nonmetal boundary, react with both acids and bases.

Why do halogens have very high electron affinities compared with other groups?

Halogens have seven valence electrons and need only one more to complete a stable noble-gas configuration; their relatively small size and high effective nuclear charge attract the incoming electron strongly, releasing a large amount of energy and giving a highly negative electron affinity.

Why is the electron affinity of fluorine slightly less negative than that of chlorine, despite fluorine being smaller?

Fluorine's very small atomic size concentrates its existing electrons closely together, so the incoming electron experiences significant repulsion from this compact electron cloud, partially offsetting the effect of fluorine's high attraction and small size, making chlorine's electron affinity slightly more negative than fluorine's.

How does effective nuclear charge explain why ionization energy generally increases across a period?

Across a period the number of shielding inner shells stays the same while the nuclear charge increases with each added proton, so each additional electron feels a stronger net pull from the nucleus, making it progressively harder to remove an electron from left to right.

Why do noble gases have positive first electron affinities?

Noble gases already have a completely filled, highly stable outer shell; adding an extra electron would force it into a new, higher-energy shell with little nuclear attraction, so energy must be supplied rather than released, giving a positive, unfavourable electron affinity.



Long Questions & Answers

Discuss the periodic trends in atomic radius, ionic radius, and ionization energy, explaining the factors that influence each property.

What factors determine atomic radius, and how does it vary across a period and down a group?

Atomic radius depends on the number of electron shells, the effective nuclear charge, and the shielding provided by inner electrons. Across a period, the number of shells stays constant while nuclear charge increases, pulling the electron cloud inward and steadily shrinking the radius. Down a group, each new element gains an entire additional shell, and the resulting increase in distance and shielding outweighs the simultaneous rise in nuclear charge, so atomic radius increases.

How does ionic radius compare with atomic radius for cations and anions?

A cation is smaller than its parent atom because losing electrons often removes an entire outer shell and leaves the remaining electrons under a stronger relative pull from the nucleus. An anion is larger than its parent atom because the added electrons increase electron-electron repulsion, causing the electron cloud to expand outward. Both cations and anions still increase in size down a group, for the same shell-addition reason that governs atomic radius.

What is ionization energy and what factors affect its magnitude?

Ionization energy is the energy required to remove an electron from a gaseous atom or ion. Its magnitude depends on effective nuclear charge, since stronger attraction raises it; atomic or ionic size, since larger size lowers it as outer electrons are held less tightly; electron arrangement, since half-filled and fully-filled subshells are extra stable and resist electron removal; the shielding effect of inner electrons, which lowers it; and spin-pair repulsion, where removing one of two paired electrons in the same orbital requires slightly less energy than removing an unpaired electron.



How does ionization energy vary across a period and down a group?

Across a period, nuclear charge increases while the number of shells stays fixed, so successive elements hold their electrons more tightly and ionization energy generally rises, reaching a maximum at the noble gas with its stable filled shell. Down a group, ionization energy decreases because atomic size and the number of shielding shells both increase, weakening the nucleus's grip on the outermost electron -- for example, in Group 1 the order is $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$.

Why do elements like boron and oxygen show exceptions to the general ionization energy trend?

Boron's first ionization energy is lower than beryllium's because beryllium has a stable, fully-filled $2s^2$ subshell, while boron's extra electron enters the higher-energy $2p$ subshell and is more easily removed. Similarly, oxygen's first ionization energy is lower than nitrogen's because nitrogen has a stable, half-filled $2p^3$ subshell, whereas oxygen's fourth p-electron must pair up in an already-occupied orbital, and the resulting electron-electron repulsion makes that paired electron easier to remove.

Explain the reactions of sodium and magnesium with water, oxygen, and chlorine, and describe how the oxides and chlorides of Period 3 elements vary in bonding character and acid-base behaviour.

How do sodium and magnesium react with water?

Sodium reacts vigorously with cold water, forming sodium hydroxide and hydrogen gas: $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$. Magnesium reacts only slowly with cold water to form magnesium hydroxide and hydrogen, but reacts much more vigorously with steam, forming magnesium oxide and hydrogen gas instead: $\text{Mg} + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{MgO} + 2\text{H}_2$. This difference reflects sodium's greater reactivity as an alkali metal compared with the alkaline earth metal magnesium.

How do sodium and magnesium react with oxygen and chlorine?

Sodium burns in oxygen with a golden-yellow flame to form a mixture of sodium oxide and sodium peroxide, and is normally stored under kerosene to prevent this reaction occurring in air. Magnesium burns in oxygen with an intense white



flame to form magnesium oxide, a reaction vigorous enough to be used in flares and fireworks. Both metals react exothermically and directly with chlorine gas to form white ionic solids: sodium chloride and magnesium chloride respectively.

How does bonding character change across the oxides and chlorides of Period 3?

Oxides and chlorides of the metals at the start of Period 3 -- sodium, magnesium, aluminium -- are predominantly ionic, existing as giant lattices held together by strong electrostatic attraction between oppositely charged ions. Moving right toward the nonmetals -- silicon, phosphorus, sulfur, chlorine -- both oxides and chlorides become increasingly covalent, existing instead as discrete molecules with comparatively weak intermolecular forces, a shift driven by the rising electronegativity of the period 3 element and the shrinking electronegativity difference with oxygen or chlorine.

What distinguishes basic, acidic, and amphoteric oxides?

A basic oxide, typically formed by a metal, reacts with water to produce an alkaline solution, as in $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$. An acidic oxide, typically formed by a nonmetal, reacts with water to produce an acidic solution, as in $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$, and also reacts with bases. An amphoteric oxide, such as Al_2O_3 , sits at the metal-nonmetal boundary and reacts with both acids and bases -- forming aluminium chloride and water with hydrochloric acid, and sodium aluminate and water with sodium hydroxide.

How are the chlorides of Period 3 classified as neutral or acidic?

Sodium chloride and magnesium chloride dissolve in water to give solutions close to neutral, since their ions simply become hydrated without reacting further with water. From aluminium chloride onward, the chlorides undergo hydrolysis: $\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + 3\text{HCl}$, releasing HCl and producing an acidic solution, a pattern that continues through silicon and phosphorus chlorides as covalent character increases.



Multiple Choice Questions (MCQs)

Which scientist arranged elements into triads, noting that the atomic weight of the middle element was roughly the average of the outer two?

- A. John Newlands
- B. Johann Dobereiner
- C. Lothar Meyer
- D. Dmitri Mendeleev

Answer: B. Johann Dobereiner

Explanation: Dobereiner's Law of Triads (1829) grouped elements such as lithium, sodium and potassium this way.

What did Moseley's X-ray work establish about the ordering of the periodic table?

- A. Elements should be ordered by atomic mass
- B. Elements should be ordered by atomic number
- C. Elements should be ordered alphabetically
- D. Elements should be ordered by density

Answer: B. Elements should be ordered by atomic number

Explanation: Moseley showed atomic number, not atomic mass, is the property the periodic law depends on, resolving ordering flaws in Mendeleev's table.

The stair-step line separating metals from nonmetals in the periodic table runs from which two elements?

- A. Carbon to lead
- B. Boron to polonium
- C. Nitrogen to bismuth
- D. Silicon to antimony

Answer: B. Boron to polonium

Explanation: The metalloid dividing line runs from boron (B) down to polonium (Po), passing through Si, Ge, As, Sb and Te.

An element in period 3 with 2 valence electrons in the s-block is:

- A. Sodium
- B. Magnesium
- C. Aluminium



D. Calcium

Answer: B. Magnesium

Explanation: Period 3, s-block, 2 valence electrons identifies magnesium ($3s^2$).

Which family of elements is described as 'salt-formers' because of their reaction with alkali and alkaline earth metals?

A. Chalcogens

B. Noble gases

C. Halogens

D. Transition metals

Answer: C. Halogens

Explanation: Halogens (Group 17) readily form salts with reactive metals, giving them the name 'salt-formers'.

Ionization energy generally increases across a period mainly because:

A. Atomic size increases

B. Shielding increases sharply

C. Effective nuclear charge increases while shielding stays roughly constant

D. The number of electron shells increases

Answer: C. Effective nuclear charge increases while shielding stays roughly constant

Explanation: Across a period, added protons increase nuclear charge while the number of inner shielding shells stays the same, so electrons are held more tightly.

Which of the following has an unusually low first ionization energy because it involves removing one of two paired electrons from the same orbital?

A. Nitrogen

B. Oxygen

C. Fluorine

D. Neon

Answer: B. Oxygen

Explanation: Oxygen's $2p^4$ configuration pairs one electron, and the resulting repulsion makes that electron easier to remove than nitrogen's stable half-filled $2p^3$.



The second electron affinity of oxygen is positive (energy absorbed) mainly because:

- A. Oxygen's nucleus is too small
- B. The incoming electron is repelled by the existing negative charge on O^-
- C. Oxygen has a full outer shell
- D. Electron affinity is always positive for nonmetals

Answer: B. The incoming electron is repelled by the existing negative charge on O^-

Explanation: Adding a second electron to an already negatively charged O^- ion requires overcoming electrostatic repulsion, so energy must be supplied.

Which oxide is amphoteric, reacting with both hydrochloric acid and sodium hydroxide?

- A. Na_2O
- B. MgO
- C. Al_2O_3
- D. SO_3

Answer: C. Al_2O_3

Explanation: Aluminium oxide (Al_2O_3) reacts with acids to form aluminium salts and with bases to form aluminates, making it amphoteric.

Which chloride of period 3 produces a solution closest to neutral (pH near 7) when dissolved in water?

- A. $AlCl_3$
- B. $SiCl_4$
- C. PCl_3
- D. $NaCl$

Answer: D. $NaCl$

Explanation: Sodium chloride simply forms hydrated ions in water without hydrolysis, giving a near-neutral solution, unlike $AlCl_3$, $SiCl_4$, and PCl_3 , which undergo hydrolysis to give acidic solutions.

Quick Revision Summary

- Modern Periodic Law: properties of elements are periodic functions of atomic number (established by Moseley, 1913)



- Dobereiner's triads (1829), Newlands' octaves (1864), Meyer's curves (1864), and Mendeleev's mass-ordered table (1869) were the key earlier attempts
- 118 elements, 7 periods, 18 groups; same group = same valence electron count = similar chemistry
- Metals (lose electrons) sit on the left and centre, nonmetals (gain electrons) on the right, metalloids along the boron-to-polonium stair-step line
- Four blocks: s-block (Groups 1-2), p-block (Groups 13-18), d-block (transition metals), f-block (lanthanides/actinides)
- Six families: alkali metals, alkaline earth metals, transition metals, chalcogens, halogens, noble gases
- Period number = shell number (n); group number = number of valence electrons for main-group elements
- Atomic radius: decreases across a period, increases down a group
- Ionic radius: cations smaller than the parent atom, anions larger; both increase down a group
- Ionization energy: increases across a period (peaking at noble gases), decreases down a group; exceptions at Be/B and N/O from subshell stability
- Electron affinity: generally more negative across a period, less negative down a group; positive for noble gases
- Electronegativity: increases across a period, decreases down a group (Pauling scale: about 0.8 for alkali metals to 4.0 for fluorine)
- Metallic character: decreases across a period, increases down a group
- Period 3 oxides and chlorides: ionic at the metal end (Na, Mg), covalent toward the nonmetal end (P, S, Cl); oxidation number matches group number

Exam Tips

- Learn the historical order (Dobereiner, then Newlands and Meyer together, then Mendeleev, then Moseley) as a timeline -- exam questions often ask 'who first...' style questions
- Remember the block-group correspondence: s-block = Groups 1-2, p-block = Groups 13-18, d-block = transition metals, f-block = lanthanides/actinides -- this single fact unlocks most electron configuration questions



- For any periodicity trend, identify which factor is changing: number of shells (down a group) or effective nuclear charge (across a period) -- most trend questions reduce to one of these two
- Watch for the two standard exceptions in ionization energy -- Be above B, and N above O -- they come from subshell stability (fully-filled and half-filled subshells), not from the general trend
- For oxide and chloride acid-base questions, classify the element first: metals at the start of a period give basic, ionic compounds; nonmetals at the end give acidic, covalent compounds; elements near the metal-nonmetal boundary, like aluminium, are often amphoteric
- Practice writing balanced equations for the reactions of Na and Mg with water, oxygen, and chlorine -- these appear directly in descriptive exam questions



Chapter 2: Atomic Structure

Every chemical property traces back to how electrons are arranged inside an atom, and this chapter builds that picture from the ground up. It starts with the atom's three fundamental particles -- protons, neutrons and electrons -- and how counting them from atomic number and mass number lets us describe both neutral atoms and ions, before turning to the experimental evidence, atomic spectra and successive ionization energies, that first revealed electrons occupy distinct shells rather than being spread randomly around the nucleus.

The second half develops the full quantum-mechanical picture: the four quantum numbers that pinpoint every electron's shell, subshell, orbital, and spin; the characteristic shapes of s, p, and d orbitals; and the three rules, the Aufbau principle, Pauli's exclusion principle, and Hund's rule, that together let us write the electronic configuration of any atom or ion. The chapter closes by connecting this configuration back to the periodic table, to species with unpaired electrons called free radicals, and to a practical application: how doping silicon's electronic configuration creates the P-type and N-type semiconductors used in modern electronics.

Learning Objectives

- Describe protons, neutrons and electrons in terms of their relative charge and relative mass
- Determine the number of protons, neutrons and electrons in atoms and ions from atomic number, mass number and charge
- Describe the behaviour of proton, neutron and electron beams moving through an electric field
- Relate quantum numbers (n , l , m , s) to the electronic distribution of elements
- Account for the variation in successive ionization energies of an element
- Apply the Aufbau principle, Pauli's exclusion principle and Hund's rule to write electronic configurations
- Describe the number of orbitals and electrons that fill s, p, d and f subshells, and the shapes of s, p and d orbitals



- Determine the electronic configuration of atoms and ions from their position in the periodic table
- Describe a free radical as a species with one or more unpaired electrons
- Explain how electronic configuration underlies the formation of P-type and N-type semiconductors

Key Concepts

2.1 Atomic Number, Mass Number, and Particle Counting

Moseley's 1913 X-ray experiments established the atomic number (Z), also called the proton number, as the fundamental identity of an element, related to the mass number (nucleon number, A) by $A = Z + N$, where N is the number of neutrons. For an atom written as A over Z X , the neutron count is found from $N = A - Z$; for example, aluminium-27 (mass number 27, atomic number 13) has 13 protons and $27 - 13 = 14$ neutrons.

For ions, the proton and neutron counts stay fixed, set by the isotope, but the electron count changes with the charge: a cation has fewer electrons than its neutral atom, equal to the positive charge lost, while an anion has more, equal to the negative charge gained. For example, aluminium-27 loses 3 electrons to form Al^{3+} , leaving $13 - 3 = 10$ electrons, while chlorine-35 gains one electron to form Cl^- , giving $17 + 1 = 18$ electrons -- confirming that atomic number and proton number are simply two names for the same concept.

2.2 Fundamental Particles and Behaviour in an Electric Field

Protons, neutrons and electrons differ in charge and mass: the proton carries a relative charge of $+1$ and a mass of 1.0073 amu, the neutron is uncharged with a very similar mass of 1.0087 amu, and the electron carries a relative charge of -1 but a mass of only about $1/1836$ that of a proton. When beams of these particles pass through an electric field at the same speed, neutrons travel straight through undeflected, protons deflect toward the negative plate, and electrons deflect toward the positive plate to a much greater extent, since they are far lighter.

The amount of deflection is described by two related, reciprocal quantities: the angle of deflection is proportional to charge divided by mass, while the radius of



the resulting circular path is proportional to mass divided by charge. This behaviour is a direct experimental consequence of each particle's charge-to-mass ratio and is one of the classic pieces of evidence for the existence and properties of subatomic particles.

2.3 Experimental Evidence for Electronic Configuration

Two independent lines of evidence reveal how electrons are arranged in shells: atomic spectra and ionization energies. Each element, when heated or subjected to an electric discharge, emits light at specific wavelengths, its atomic emission spectrum, and absorbs exactly those same wavelengths from white light passed through its vapour, its atomic absorption spectrum -- because every element has a unique set of electron energy levels, its spectrum acts as a fingerprint that identifies it.

Successive ionization energies, the energy needed to remove the 1st, 2nd, 3rd electron and so on from an atom one at a time, provide direct evidence for shell structure: plotting these values for magnesium shows two large jumps, once after the 2nd electron, where the outer shell is exhausted, and again after the 10th, where the middle shell is exhausted, confirming three distinct electron shells. Separately, comparing the first ionization energies of different elements across the periodic table shows the now-familiar trends: ionization energy decreases down a group as shells and shielding increase, and increases across a period as nuclear charge grows while shell number stays fixed, with alkali metals lowest and noble gases highest in each period.

2.4 Quantum Numbers

Since Schrodinger's wave model treats the electron as occupying three-dimensional space, three quantum numbers are needed to describe each orbital. The principal quantum number ($n = 1, 2, 3, \dots$), labelled K, L, M, N, describes the shell's size and energy and sets its maximum electron capacity at $2n^2$. The azimuthal quantum number ($l = 0$ to $n-1$), labelled s, p, d, f, describes the subshell's shape, with the number of electrons a subshell can hold given by $2(2l+1)$: 2 for s, 6 for p, 10 for d, and 14 for f.

The magnetic quantum number (m , ranging from $-l$ through 0 to $+l$) describes an orbital's orientation in space within its subshell, and the number of allowed



values of m equals the number of orbitals in that subshell: one for s , three for p , five for d , and seven for f -- orbitals of the same subshell, called degenerate orbitals, share the same energy. A fourth quantum number, spin ($s = +1/2$ or $-1/2$), distinguishes the two electrons that can occupy the same orbital, since the three spatial quantum numbers alone cannot tell them apart.

2.5 Shapes of Atomic Orbitals

An atomic orbital is the three-dimensional region around the nucleus where an electron is most likely to be found. The s orbital is spherical, with its electron density spread uniformly in all directions, and grows larger as the principal quantum number increases. The p orbitals, p_x , p_y , and p_z , each have two lobes arranged along one of the three perpendicular axes, giving a dumbbell shape rather than spherical symmetry.

The five d orbitals have more complex shapes: d_{xy} , d_{xz} , and d_{yz} each lie between a pair of axes with four lobes, $d_{x^2-y^2}$ has four lobes lying along the x and y axes themselves, and d_{z^2} has two lobes along the z -axis plus a ring of density in the xy plane. The seven f orbitals have still more complicated shapes, but like all orbitals of the same subshell, they are degenerate, equal in energy in the absence of an external field.

2.6 Electronic Configuration: Aufbau, Pauli, and Hund

Electronic configuration describes how electrons are distributed among shells, subshells, and orbitals. The Aufbau, or building-up, principle states that subshells fill in order of increasing energy, determined by the sum ($n + l$): a subshell with a lower ($n + l$) value fills first, and when two subshells share the same ($n + l$) value, the one with the lower n fills first -- explaining why $4s$ ($n + l = 4$) fills before $3d$ ($n + l = 5$), giving the familiar order $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s$.

Two further rules govern how electrons occupy orbitals within a subshell. Pauli's exclusion principle states that no two electrons in an atom can share all four quantum numbers, so any two electrons occupying the same orbital must have opposite spins. Hund's rule states that when degenerate orbitals, such as the three p orbitals, are available, electrons occupy separate orbitals singly, with



parallel spins, before any orbital receives a second electron, minimizing electron-electron repulsion and giving the lowest-energy, most stable arrangement.

2.7 Electronic Configuration and the Periodic Table

An element's position in the periodic table directly mirrors its electronic configuration: elements in Groups 1 and 2 are filling an ns subshell, elements in Groups 13-18 are filling an np subshell, the transition metals in the middle block are filling an $(n-1)d$ subshell, and the lanthanides and actinides below the main table are filling an $(n-2)f$ subshell -- and since these subshells hold a maximum of 2, 6, 10, and 14 electrons respectively, they define the exact widths of the s-block, p-block, d-block, and f-block.

The electrons in an atom's outermost shell, its valence electrons, are primarily responsible for chemical behaviour, and elements in the same group share the same valence-shell configuration pattern, such as ns^1 for Group 1 or ns^2np^1 for Group 13, which is why they show similar chemical properties. Because this pattern can be read directly from an element's row and column, a full or valence electron configuration can be deduced from the periodic table without memorization.

2.8 Electronic Configuration of Ions and Free Radicals

Positive ions form when atoms lose electrons, and negative ions form when atoms gain electrons; in both cases the resulting configuration often matches that of the nearest noble gas -- Na^+ (10 electrons) has the configuration of neon, and S^{2-} (18 electrons) has the configuration of argon. For main-group elements, electrons are lost from the outermost subshell first, but d-block elements behave differently: although the $4s$ subshell fills before $3d$ when building up an atom, electrons are lost from $4s$ first when a d-block atom forms a cation, so titanium ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$) forms Ti^{2+} by losing both $4s$ electrons, giving $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$.

A free radical is a species with one or more unpaired electrons, such as the free chlorine atom, configuration $1s^2 2s^2 2p^6 3s^2 3p^5$, which has one unpaired electron in its $3p$ subshell, or polyatomic radicals such as OH and CH_3 . Free radicals are typically highly reactive because an unpaired electron readily seeks a partner to pair with in a new bond.



2.9 Electronic Configuration and Semiconductors

Semiconductors are materials whose ability to conduct electricity depends on their specific electronic configuration. Pure silicon, electron configuration 2, 8, 4, has four valence electrons and forms four bonds to neighbouring silicon atoms in its crystal lattice, leaving no free charge carriers and therefore no conduction pathway in its pure form.

Doping silicon with trivalent impurity atoms such as aluminium, with 3 valence electrons, creates electron-deficient holes that act as positive charge carriers, producing a P-type semiconductor, while doping with pentavalent impurity atoms such as phosphorus, with 5 valence electrons, contributes extra, loosely-held electrons that act as negative charge carriers, producing an N-type semiconductor -- both are the basis of the diodes and transistors used in modern electronic devices.

Important Definitions

What is atomic number (proton number)?

The number of protons in the nucleus of an atom; it is the fundamental property that defines an element's identity.

What is mass number (nucleon number)?

The total number of protons and neutrons in the nucleus of an atom, related to atomic number by $A = Z + N$.

What is the principal quantum number (n)?

A positive integer describing the size and energy of a shell; the maximum number of electrons it can hold is $2n^2$.

What is the azimuthal quantum number (l)?

A quantum number ranging from 0 to $(n-1)$ that describes the shape of a subshell, designated s, p, d, or f.

What is the magnetic quantum number (m)?

A quantum number ranging from $-l$ to $+l$ that describes the spatial orientation of an individual orbital within a subshell.

What is the spin quantum number (s)?



A quantum number with value $+1/2$ or $-1/2$ that distinguishes the two electrons that can occupy the same orbital.

What is the Aufbau principle?

The principle that subshells fill with electrons in order of increasing energy, found using the $(n + l)$ rule.

What is Pauli's exclusion principle?

No two electrons in an atom can have identical values for all four quantum numbers, so electrons sharing an orbital must have opposite spins.

What is Hund's rule?

When degenerate orbitals are available, electrons occupy separate orbitals singly, with parallel spins, before any orbital is doubly occupied.

What is a free radical?

A species that has one or more unpaired electrons, making it typically highly reactive.

Key Facts and Relations

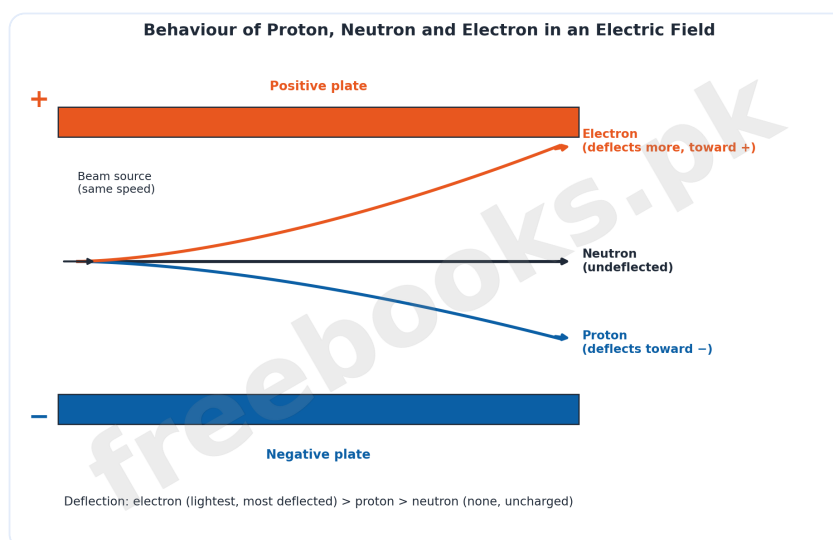
Topic	Key Fact / Relation
Mass/nucleon number relation	$A = Z + N$, so $N = A - Z$
Maximum electrons in a shell	$2n^2$ (K=2, L=8, M=18, N=32)
Electrons in a subshell	$2(2l+1)$: s=2, p=6, d=10, f=14
Orbitals in a subshell	$(2l+1)$: s=1, p=3, d=5, f=7
Angle of deflection in an electric field	Proportional to charge / mass
	Proportional to mass / charge



Topic	Key Fact / Relation
Radius of deflection in an electric field	
Aufbau filling order	$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$
Na ⁺ electronic configuration	$1s^2 2s^2 2p^6$ (same as neon)
S ²⁻ electronic configuration	$1s^2 2s^2 2p^6 3s^2 3p^6$ (same as argon)
d-block cation rule	4s electrons are lost before 3d electrons when a transition metal forms a cation

Diagrams

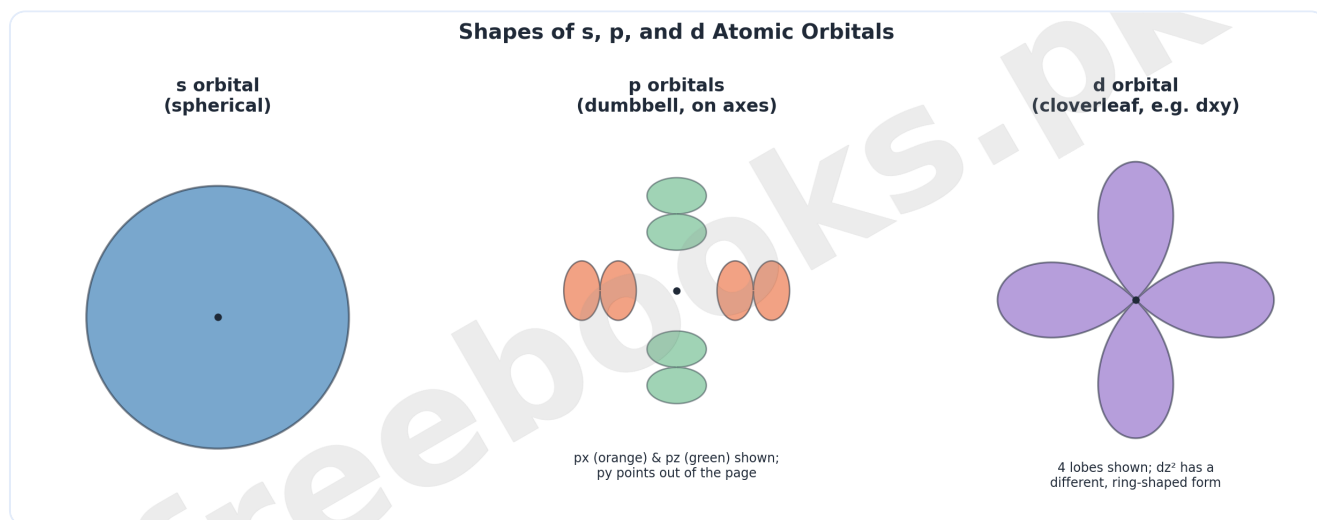
Behaviour of Proton, Neutron and Electron in an Electric Field: Three particle paths passing between charged plates: the neutron travels straight, the proton deflects toward the negative plate, and the electron deflects sharply toward the positive plate



Behaviour of Proton, Neutron and Electron in an Electric Field

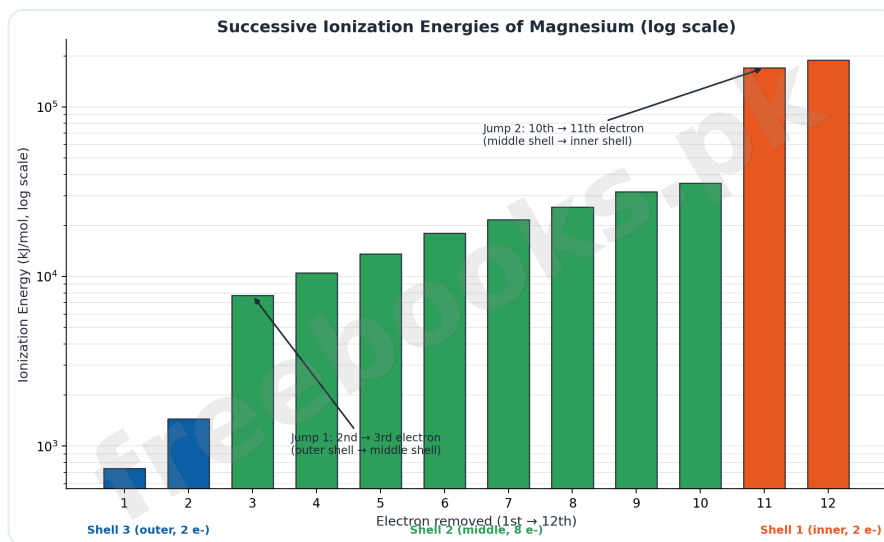


Shapes of s, p, and d Atomic Orbitals: A spherical s orbital, dumbbell-shaped p orbitals lying along perpendicular axes, and the characteristic four-lobed cloverleaf shape of a d orbital



Shapes of s, p, and d Atomic Orbitals

Successive Ionization Energies of Magnesium: A log-scale plot of the twelve successive ionization energies of magnesium against the number of electrons removed, showing two large jumps that reveal its three electron shells



Successive Ionization Energies of Magnesium

Short Questions & Answers

Why does an electron deflect more than a proton when both pass through the same electric field at the same speed?



Deflection depends on the charge-to-mass ratio; although the electron and proton carry equal and opposite charge magnitudes, the electron's mass is about 1/1836 that of the proton, giving it a far larger charge-to-mass ratio and therefore a much greater deflection toward the positive plate.

What do the two large jumps in magnesium's successive ionization energy graph reveal?

They mark the points where electron removal moves to a shell that is closer to the nucleus -- the first jump occurs after the 2nd electron, once the outer shell is exhausted, and the second after the 10th, once the middle shell is exhausted, together confirming magnesium's electrons occupy three distinct shells.

Why is the third ionization energy of magnesium so much larger than its second?

The first two electrons are removed from magnesium's outer, third shell, but the third electron must be removed from the full, more tightly-bound second shell that is much closer to the nucleus, requiring far more energy.

Why does the 4s subshell fill before the 3d subshell according to the Aufbau principle?

The $(n + l)$ value for 4s is $4 + 0 = 4$, while for 3d it is $3 + 2 = 5$; since a lower $(n + l)$ value means lower energy, 4s fills first even though its principal quantum number is higher than 3d's.

Why do transition metal atoms lose their 4s electrons before their 3d electrons when forming cations?

Once the 3d subshell is occupied, its effective energy drops below that of 4s in the resulting ion, so the 4s electrons, now higher in energy, are removed first, even though 4s filled before 3d when the atom was originally built up.

How many orbitals and electrons can a d subshell hold, and why?

A d subshell has $l = 2$, giving $2l + 1 = 5$ orbitals, each holding up to 2 electrons, for a maximum of $2(2l+1) = 10$ electrons in total.

What does Hund's rule say about filling the three 2p orbitals of carbon, nitrogen, and oxygen?

Electrons occupy separate degenerate orbitals singly, with parallel spins, before any orbital is doubly occupied; carbon's two 2p electrons therefore sit in separate orbitals, and only oxygen's fourth 2p electron is forced to pair up.



Why is a free chlorine atom classed as a free radical?

Its configuration, $1s^2 2s^2 2p^6 3s^2 3p^5$, leaves one 3p electron unpaired, and a species with one or more unpaired electrons is defined as a free radical.

Why does silicon conduct no electricity in its pure crystalline form?

Each silicon atom has four valence electrons and forms four covalent bonds to its neighbours, using up all its valence electrons in bonding and leaving no free charge carriers to conduct current.

What is the difference between a P-type and an N-type semiconductor?

A P-type semiconductor is formed by doping with a trivalent impurity such as aluminium, creating electron-deficient holes that carry positive charge; an N-type semiconductor is formed by doping with a pentavalent impurity such as phosphorus, which contributes extra, loosely-held electrons that carry negative charge.

Long Questions & Answers

Describe the evidence for electronic shell structure provided by successive ionization energies, and explain how quantum numbers describe the arrangement of electrons within those shells.

What are successive ionization energies, and how do they provide evidence for electron shells?

Successive ionization energies are the energies required to remove the 1st, 2nd, 3rd, and further electrons from an atom, one at a time. Because each removed electron leaves behind a smaller, more positively charged ion, successive values always increase; but large jumps occur specifically when an electron must be removed from a shell that is closer to the nucleus, and these jumps reveal exactly how many electrons occupy each shell.

How does the graph of magnesium's successive ionization energies confirm three electron shells?

Plotting magnesium's twelve successive ionization energies against the number of electrons removed shows a gradual rise for the first two electrons in the outer shell, a large jump for the third electron entering the middle shell, a gradual rise



through electrons three to ten, and a much larger jump for the eleventh electron entering the innermost shell -- two large jumps confirming three distinct shells.

What is the principal quantum number, and what does it describe?

The principal quantum number, n , takes positive integer values 1, 2, 3 and so on, and describes the size and energy of a shell; larger n means a greater average distance from the nucleus, higher energy, and a maximum electron capacity of $2n^2$ for that shell.

What do the azimuthal and magnetic quantum numbers describe?

The azimuthal quantum number, l , ranges from 0 to $(n - 1)$ and describes the shape of a subshell, s, p, d, or f; the magnetic quantum number, m , ranges from $-l$ to $+l$ and describes the spatial orientation of each individual orbital within that subshell.

Why is a fourth quantum number needed, and what does it describe?

The three quantum numbers n , l , and m fully describe an orbital's size, shape, and orientation, but each orbital can hold two electrons; the spin quantum number, s , with values of $+1/2$ or $-1/2$, is needed to distinguish between these two electrons, which must have opposite spins according to Pauli's exclusion principle.

Explain the Aufbau principle, Pauli's exclusion principle, and Hund's rule, and describe how they are applied to write the electronic configuration of an atom.

What does the Aufbau principle state, and how is the filling order determined?

The Aufbau principle states that subshells fill with electrons in order of increasing energy. This order is found using the $(n + l)$ rule: a subshell with a lower $(n + l)$ sum is filled first, and if two subshells share the same sum, the one with the lower n value fills first, giving the sequence 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.



What does Pauli's exclusion principle state?

No two electrons in the same atom can have identical values for all four quantum numbers; in practice, this means any orbital, fully specified by n , l , and m , can hold at most two electrons, and those two electrons must have opposite spin quantum numbers.

What does Hund's rule state, and why does it apply?

When degenerate orbitals of equal energy are available, electrons occupy them singly, with parallel spins, before any orbital receives a second electron; this minimizes the electron-electron repulsion that would otherwise occur if two electrons were forced into the same orbital, giving the atom its lowest-energy, most stable configuration.

How are these three rules applied together to write an atom's electronic configuration?

Electrons are added one at a time following the Aufbau energy order; each orbital is checked against Pauli's exclusion principle so no orbital exceeds two electrons of opposite spin; and whenever a subshell has multiple degenerate orbitals available, Hund's rule is applied so each orbital gains one electron before any is doubly occupied.

Why do d-block elements form an exception when they lose electrons to form ions?

Although the Aufbau ($n + l$) rule fills 4s before 3d when building up a neutral atom, once electrons occupy the 3d subshell its energy drops below that of the now-outermost 4s subshell in the resulting species, so 4s electrons, being higher in energy in the ion, are always removed first when a transition metal atom forms a cation.

Multiple Choice Questions (MCQs)

An atom of an element X has atomic number Z and mass number A. The number of neutrons in this atom is:



- A. $Z + A$
- B. $A - Z$
- C. $Z - A$
- D. $A \times Z$

Answer: B. $A - Z$

Explanation: $N = A - Z$, since mass number equals the sum of protons and neutrons.

When beams of protons, neutrons and electrons pass through an electric field at the same speed, which particle is undeflected?

- A. Proton
- B. Neutron
- C. Electron
- D. All are deflected equally

Answer: B. Neutron

Explanation: Neutrons carry no charge, so they experience no force in an electric field and travel straight through.

The two large jumps in magnesium's successive ionization energy graph occur after removing which electrons?

- A. 1st and 2nd
- B. 2nd and 10th
- C. 3rd and 11th
- D. 8th and 10th

Answer: B. 2nd and 10th

Explanation: The jumps occur after the 2nd electron, leaving the outer shell, and after the 10th, leaving the middle shell, confirming three shells.

The maximum number of electrons a p subshell can hold is:

- A. 2
- B. 6
- C. 10
- D. 14

Answer: B. 6

Explanation: A p subshell has $l = 1$, giving $2(2l+1) = 6$ electrons across 3 orbitals.

According to the Aufbau ($n + l$) rule, which subshell is filled first?



- A. 4s ($n+l=4$)
- B. 3d ($n+l=5$)
- C. 4p ($n+l=5$)
- D. 4d ($n+l=6$)

Answer: A. 4s ($n+l=4$)

Explanation: 4s has the lowest ($n+l$) value of 4, so it fills before 3d and 4p, both of which equal 5.

Pauli's exclusion principle states that two electrons occupying the same orbital must have:

- A. The same spin
- B. Opposite spins
- C. The same value of l
- D. Different values of n

Answer: B. Opposite spins

Explanation: No two electrons in an atom can share all four quantum numbers, so two electrons in the same orbital, sharing n , l , and m , must differ in spin.

According to Hund's rule, three electrons filling three degenerate p orbitals will:

- A. Pair up in one orbital first
- B. Occupy separate orbitals with parallel spins
- C. Occupy separate orbitals with opposite spins
- D. Skip the p orbitals entirely

Answer: B. Occupy separate orbitals with parallel spins

Explanation: Hund's rule places one electron in each degenerate orbital, with parallel spins, before any pairing occurs.

The electronic configuration of Na^+ is the same as that of which noble gas?

- A. Helium
- B. Neon
- C. Argon
- D. Krypton

Answer: B. Neon

Explanation: Na^+ has 10 electrons ($1s^2 2s^2 2p^6$), identical to neon's configuration.



When a transition metal atom such as titanium forms a cation, which electrons are lost first?

- A. 3d electrons
- B. 4s electrons
- C. 1s electrons
- D. 2p electrons

Answer: B. 4s electrons

Explanation: Despite filling after 3d in the neutral atom, 4s electrons become higher in energy once 3d is occupied, so they are lost first when the ion forms.

A P-type semiconductor is formed by doping pure silicon with an impurity that has how many valence electrons?

- A. 3
- B. 4
- C. 5
- D. 8

Answer: A. 3

Explanation: Trivalent impurities such as aluminium, with 3 valence electrons, create electron-deficient holes that act as positive charge carriers, forming a P-type semiconductor.

Quick Revision Summary

- Atomic number (Z) = proton number = number of protons; defines an element's identity
- Mass number (A) = nucleon number = protons + neutrons; $N = A - Z$
- Ion electron count: cation = protons - charge; anion = protons + charge (proton and neutron count unchanged)
- In an electric field: neutrons undeflected, protons deflect toward the negative plate, electrons deflect more toward the positive plate
- Angle of deflection is proportional to charge/mass; radius of deflection is proportional to mass/charge
- Atomic spectra (emission and absorption) act as an element's fingerprint, unique to its electron energy levels
- Successive ionization energies show large jumps between shells; first ionization energies across elements show the standard periodic trends



- Principal quantum number (n): shell size/energy, max electrons = $2n^2$
- Azimuthal quantum number (l): subshell shape (s, p, d, f); electrons per subshell = $2(2l+1)$
- Magnetic quantum number (m): orbital orientation; orbitals per subshell = $2l+1$
- Spin quantum number (s): $+1/2$ or $-1/2$, distinguishes the 2 electrons in one orbital
- Aufbau principle: fill lowest (n+l) first, lower n breaks ties | Pauli's principle: max 2 electrons per orbital, opposite spins | Hund's rule: singly occupy degenerate orbitals first
- Valence electron configuration repeats down a group, explaining similar chemical properties; blocks (s, p, d, f) match the subshell being filled
- d-block cations lose 4s electrons before 3d electrons; free radicals have 1 or more unpaired electrons; semiconductor type depends on dopant valence electron count (3 for P-type, 5 for N-type)

Exam Tips

- Practice the (n+l) rule directly -- most Aufbau-order exam questions can be solved by comparing two (n+l) sums rather than memorizing the whole sequence
- When counting electrons in an ion, always start from the neutral atom's proton count, then add electrons for a negative charge or subtract for a positive charge -- protons and neutrons never change
- Remember the special order-of-removal rule for d-block cations: it is the opposite of the order of filling (4s comes out first, even though it filled first)
- For Hund's rule questions, draw the orbital boxes and fill them singly, left to right, before pairing any -- this avoids common configuration mistakes for elements like carbon, nitrogen, and oxygen
- Link quantum numbers to real quantities: n to shell size/energy, l to subshell shape, m to orbital orientation, s to which of the two electrons in an orbital
- Successive ionization energy graphs are a favourite exam diagram -- practice explaining WHY each jump occurs (a shell change) rather than just describing that a jump happens



Chapter 3: Chemical Bonding

Chemical bonding explains why substances have the properties they do, and this chapter builds a full toolkit for understanding it. It starts with the three core Lewis-theory bond types, ionic, covalent, and dative, and with polyatomic ions whose central atoms expand beyond a normal octet, before turning to electronegativity as the single quantity that predicts whether a bond will be nonpolar covalent, polar covalent, or ionic, and to dipole moment as the measurable consequence of that polarity.

The second half develops three complementary models used to explain and predict molecular structure and bonding: Valence Bond Theory, which describes covalent bonds as the overlap of atomic orbitals into sigma and pi bonds, often after hybridization into sp , sp^2 , or sp^3 orbitals; the VSEPR model, which predicts a molecule's three-dimensional shape and bond angles purely from the number of bonding and lone electron pairs around its central atom, with real applications in drug design; and Molecular Orbital Theory, which explains subtler effects such as oxygen's paramagnetism that simpler theories cannot, using the concept of bond order.

Learning Objectives

- Analyze the formation of dative bonds in CO, ozone, and the H_3O^+ ion
- Recognize that polyatomic ions such as sulfate and nitrate can have expanded octets
- Use electronegativity differences to predict whether a bond is ionic or covalent
- Use electronegativity to explain bond polarity and the dipole moments of molecules
- Describe the shapes and bond angles of molecules and ions using VSEPR theory, including its role in drug design
- Explain valence bond theory and describe covalent bonding using sp , sp^2 , and sp^3 hybridization



- Explain the salient features of molecular orbital theory and the paramagnetic nature of the oxygen molecule
- Calculate the bond order of N_2 , O_2 , F_2 , and He_2
- Describe van der Waals forces and hydrogen bonding, and use hydrogen bonding to explain the anomalous properties of water
- Use bond energy and bond length values to compare the reactivity and strength of covalent molecules

Key Concepts

3.1 Types of Chemical Bonds: Ionic, Covalent, and Dative

According to Lewis theory, atoms bond to complete their outermost shell with a noble-gas-like configuration, usually an octet. An ionic bond forms by the complete transfer of one or more electrons from an atom of low ionization energy to an atom of high electron affinity, as when sodium (2,8,1) loses its outer electron to become Na^+ (2,8), matching neon's configuration, while chlorine (2,8,7) gains that electron to become Cl^- (2,8,8), matching argon's; the oppositely charged ions then attract each other strongly in the crystal lattice. A covalent bond, by contrast, forms by the mutual sharing of an electron pair between two atoms, each completing its own valence shell; the bond is nonpolar when the two atoms have identical electronegativity, as in Cl_2 , and polar when they differ, as in H-Cl .

A dative, or coordinate covalent, bond forms when one atom alone supplies both electrons of the shared pair: an electron-rich donor atom with a lone pair bonds to an electron-deficient acceptor. In the hydronium ion, H_3O^+ , a lone pair on the oxygen of water is donated to a bare proton; in carbon monoxide, oxygen forms a normal double bond to carbon and then donates a further lone pair to satisfy carbon's octet; and in ozone, O_3 , one oxygen atom donates a lone pair to a second oxygen atom, bonded as a free radical, forming a coordinate bond that leaves the donor atom with a formal positive charge and the acceptor atom a formal negative charge.



3.2 Expanded Octets in Polyatomic Ions

Polyatomic ions are composed of more than one type of atom and mostly carry a negative charge, common examples being carbonate, sulfate, and nitrate. In some of these ions, such as sulfate (SO_4^{2-}), the central atom exceeds the normal octet by using its available d orbitals to accommodate extra electron density; the number of valence electrons around the central atom can be counted directly from its Lewis structure as 2 times the number of double-bond electron pairs plus 2 times the number of single-bond electron pairs or lone pairs, and for sulfate this comes to 12 electrons, four more than a normal octet. This expansion, seen also in ions such as ClO_4^- and the tri-iodide ion I_3^- which expands to 10 electrons around its central iodine, is only possible for elements from period 3 onward, since period 2 elements have no accessible d orbitals to expand into.

3.3 Electronegativity, Bond Type, and Bond Polarity

The difference in electronegativity between two bonded atoms is a reliable predictor of bond type: a difference below about 0.4 gives a nonpolar covalent bond, a difference between 0.4 and 1.8 gives a polar covalent bond, and a difference above 1.8 gives an ionic bond. This scale is illustrated by the electronegativity differences of H-H (0, nonpolar), H-Cl (0.9, polar covalent), and NaCl (2.1, ionic) -- exactly matching their observed bonding character.

3.4 Dipole Moment and Molecular Polarity

When two bonded atoms differ in electronegativity, the shared electron density shifts toward the more electronegative atom, leaving a partial positive charge on one atom and a partial negative charge on the other; a molecule with this separation of charge is called a dipole, and the size of the separation is its dipole moment, measured in Debye units, with a higher value indicating greater polarity. For molecules of more than two atoms, the overall dipole moment depends on molecular geometry: water's V-shaped structure gives it a net dipole moment of 1.85 D directed from the hydrogen end toward the oxygen end, and the fact that this value is nonzero is itself evidence that water is bent rather than linear.



Some molecules have individually polar bonds yet a net dipole moment of zero, because their symmetric geometry causes the individual bond moments to cancel exactly: BeCl_2 is linear with its two Be-Cl moments pointing in opposite directions, BF_3 is trigonal planar with its three B-F moments cancelling, and CCl_4 is perfectly tetrahedral with its four C-Cl moments cancelling, making all three molecules nonpolar overall despite having polar bonds. As a general rule, a molecule with identical ligands arranged in a regular, symmetric geometry around the central atom will have zero net dipole moment.

3.5 Bond Energy, Bond Length, and Relative Bond Strengths

Bond energy is the average energy required to break one mole of a particular bond, and it measures both bond strength and reactivity; it rises with increasing electronegativity difference between the bonded atoms, for example H-F at 565 kJ/mol is far stronger than H-I at 295 kJ/mol, and multiple bonds are always stronger than single bonds between the same two atoms (C triple-bond C is stronger than C=C, which is stronger than C-C). Bond length, the distance between two bonded nuclei, generally increases with the size of the bonded atoms, C-Cl at 180 pm is longer than C-F at 135 pm, and decreases as electronegativity difference increases, since the resulting ionic character pulls the atoms closer together.

Comparing bond energies across bond types confirms that true chemical bonds are far stronger than intermolecular forces: the ionic bond in NaCl (760 kJ/mol) and the covalent O-H bond in water (464 kJ/mol) both dwarf hydrogen bonding (20-50 kJ/mol), permanent dipole-dipole forces (5-20 kJ/mol), and London dispersion forces (1-20 kJ/mol); the metallic bond, at around 100-150 kJ/mol, sits between these two groups, its relative weakness attributed to the extensive delocalization of electrons throughout the metallic crystal.

3.6 Valence Bond Theory: Sigma and Pi Bonds

Valence Bond Theory (VBT) explains covalent bond formation, not just molecular shape: a bond forms when two half-filled atomic orbitals of similar energy, one from each atom, overlap along the line joining their nuclei, and a greater degree of overlap produces a stronger, more directional bond. A sigma bond forms by this kind of head-on, linear overlap, s-s overlap as in H_2 , s-p overlap as in HCl, or



p-p overlap along the same axis as in Cl_2 , and is the only type of bond present in every single covalent bond, single or multiple.

A pi bond forms differently: when two p orbitals on adjacent atoms are aligned parallel to each other rather than head-on, their sideways overlap creates two regions of electron density, one above and one below the line joining the nuclei. A double bond, such as in O_2 , therefore consists of one sigma bond, from head-on overlap of one pair of p orbitals, plus one pi bond, from sideways overlap of a second, perpendicular pair; a triple bond, such as in N_2 , consists of one sigma bond plus two pi bonds, using all three p orbitals on each atom.

3.7 Atomic Orbital Hybridization

Hybridization is the mixing of atomic orbitals of comparable energy within a single atom to form a new set of equivalent orbitals of identical energy and shape, with the number of hybrid orbitals produced always equal to the number of atomic orbitals mixed. In sp hybridization, one s and one p orbital mix to give two sp orbitals arranged linearly at 180 degrees, explaining the linear geometry of BeCl_2 ; in sp² hybridization, one s and two p orbitals mix to give three sp² orbitals arranged in a trigonal plane at 120 degrees, explaining the shape of BF_3 .

In sp³ hybridization, one s and three p orbitals mix to give four sp³ orbitals arranged tetrahedrally, explaining the shape of methane, CH_4 , where each of the four sp³ orbitals of carbon overlaps with a hydrogen 1s orbital to form a sigma bond directed toward a corner of a regular tetrahedron. In every case, hybrid orbitals have lower energy than the unhybridized atomic orbitals they replace, and the resulting hybrid-orbital geometry, linear for sp, trigonal planar for sp², tetrahedral for sp³, directly matches the electron-pair geometry predicted independently by the VSEPR model.

3.8 VSEPR Theory: Predicting Molecular Shapes

The Valence Shell Electron Pair Repulsion (VSEPR) model, proposed by Sidgwick and Powell, predicts a molecule's shape from the idea that all electron pairs around a central atom, bonding and lone pairs alike, arrange themselves as far apart as possible to minimize repulsion. Because lone pairs occupy more space than bond pairs, the strength of repulsion follows the order lone pair-lone pair greater than lone pair-bond pair greater than bond pair-bond pair, so a lone pair



always compresses the bond angles around it below the ideal geometric value: ammonia's bond angle is compressed from the ideal 109.5 degrees to 107 degrees by one lone pair, and water's is compressed further, to 104.5 degrees, by two.

The total number of electron pairs around the central atom sets the electron-pair geometry, 2 pairs give linear, 3 give trigonal planar, 4 give tetrahedral, 5 give trigonal bipyramidal, and 6 give octahedral, while the molecule's actual shape is this same geometry with any lone-pair positions left out of the description -- so four electron pairs give a tetrahedral shape with zero lone pairs (CH_4), a pyramidal shape with one lone pair (NH_3), and a bent, V-shaped molecule with two lone pairs (H_2O). A double or triple bond, despite containing two or three electron pairs, is still treated as a single region of electron density for VSEPR purposes.

3.9 VSEPR in Drug Design

Drugs act on specific biological targets, such as enzyme active sites, through bioactive molecules called ligands, and a drug's effectiveness depends heavily on its molecular shape fitting its target the way a key fits a lock, a property called specificity. Because VSEPR theory predicts the three-dimensional shape and bond angles of a molecule directly from its structure, it is a practical tool in drug design for judging whether a candidate ligand's shape is compatible with a target's active site; aspirin, for example, binds to and blocks the enzyme cyclooxygenase (COX) because the shape of its acetyl group is complementary to the shape of COX's active site.

3.10 Molecular Orbital Theory: Bond Order and Paramagnetism

Molecular Orbital Theory (MOT) treats a molecule's electrons as occupying molecular orbitals belonging to the whole molecule, formed when atomic orbitals of matching sign overlap. Two atomic orbitals always combine to give two molecular orbitals: a lower-energy bonding orbital, sigma or pi, when same-sign lobes overlap, and a higher-energy antibonding orbital, sigma-star or pi-star, when opposite-sign lobes overlap. Bond order, a measure of the number of bonds between two atoms, is calculated as half the difference between the number of



electrons in bonding orbitals and the number in antibonding orbitals; a bond order of zero, as calculated for He_2 , means the molecule does not form at all.

Applying this method to N_2 gives a bond order of 3, one sigma and two pi bonds, consistent with its known triple bond and very high bond energy, while O_2 gives a bond order of 2, one sigma and one pi bond, a double bond, but MOT reveals something VBT cannot: oxygen's molecular orbital diagram places two of its electrons singly, with parallel spins, in two separate antibonding pi-star orbitals. These two unpaired electrons make O_2 paramagnetic, meaning it is attracted into a magnetic field, a real, experimentally observed property, liquid oxygen visibly clings between the poles of a strong magnet, that simpler bonding theories fail to predict.

Important Definitions

What is a dative (coordinate covalent) bond?

A covalent bond in which both shared electrons are donated by only one of the two bonding atoms.

What is an expanded octet?

A central atom having more than eight electrons in its valence shell, made possible by involvement of available d orbitals, as in SO_4^{2-} .

What is a dipole moment?

A quantitative measure, in Debye units, of the separation of partial positive and partial negative charge in a polar bond or molecule.

What is bond energy?

The average energy required to break all bonds of a particular type in one mole of a substance.

What is bond length?

The distance between the nuclei of two atoms joined by a covalent bond.

What is a sigma bond?

A covalent bond formed by the head-on, linear overlap of two atomic orbitals along the axis joining their nuclei.

What is a pi bond?



A covalent bond formed by the sideways overlap of two parallel p orbitals, with electron density above and below the internuclear axis.

What is hybridization?

The mixing of atomic orbitals of comparable energy within one atom to form a new set of equivalent orbitals of identical energy and shape.

What is bond order in molecular orbital theory?

Half the difference between the number of electrons in bonding molecular orbitals and the number in antibonding molecular orbitals.

What does it mean for a substance to be paramagnetic?

It has one or more unpaired electrons and is therefore attracted into an external magnetic field.

Key Facts and Relations

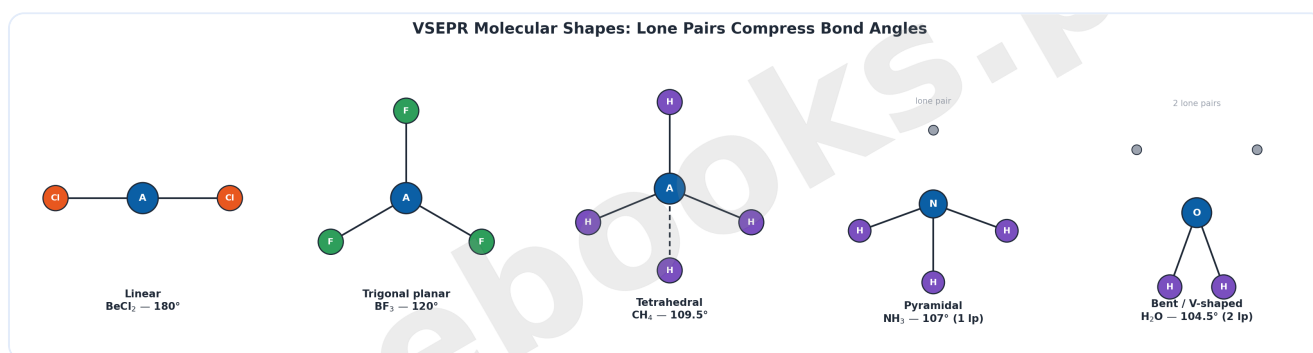
Topic	Key Fact / Relation
Bond-type prediction by electronegativity difference	Below 0.4: nonpolar covalent 0.4-1.8: polar covalent above 1.8: ionic
Valence electrons around a central atom (Lewis structure)	2 x (double-bond electron pairs) + 2 x (single-bond pairs or lone pairs)
Bond order (MOT)	$\text{Bond order} = (\text{bonding electrons} - \text{antibonding electrons}) / 2$
Bond order of N ₂	3 (one sigma + two pi bonds)
Bond order of O ₂	2 (one sigma + one pi bond); paramagnetic, 2 unpaired electrons in pi* orbitals
Bond order of He ₂	0 (molecule does not form)
VSEPR: 4 pairs, 0 lone pairs	Tetrahedral shape, 109.5 degrees, e.g. CH ₄
VSEPR: 4 pairs, 1 lone pair	Pyramidal shape, about 107 degrees, e.g. NH ₃
VSEPR: 4 pairs, 2 lone pairs	Bent/V-shaped, about 104.5 degrees, e.g. H ₂ O
Relative bond strength (kJ/mol)	



Topic	Key Fact / Relation
	Ionic (NaCl, 760) > covalent (O-H, 464) > hydrogen bond (20-50) > dipole-dipole (5-20) > London dispersion (1-20)

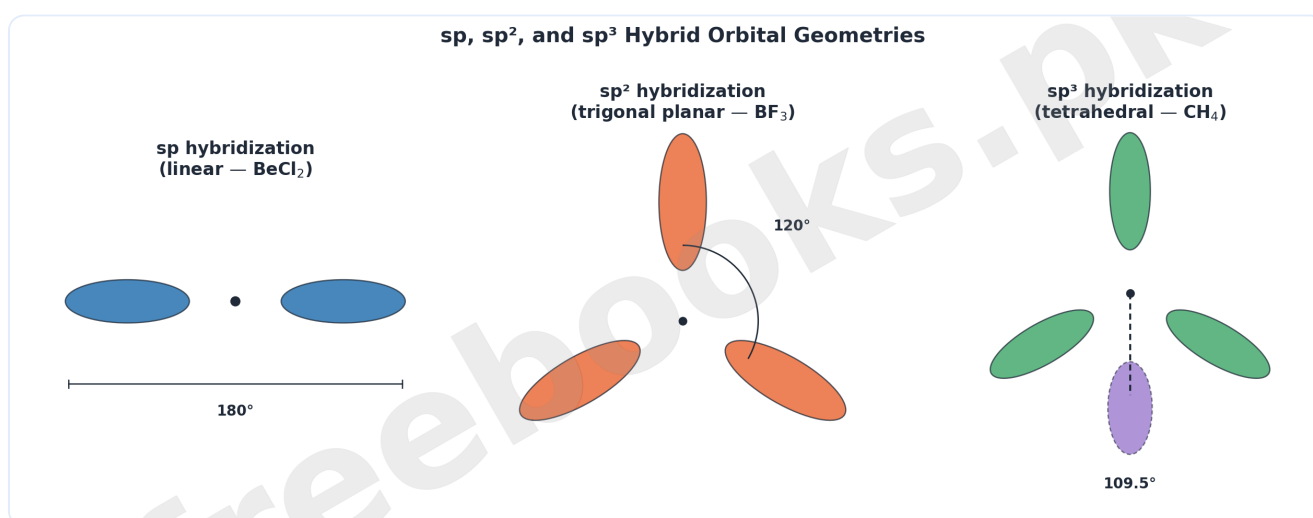
Diagrams

VSEPR Molecular Shapes: A comparison of five VSEPR shapes, linear (BeCl_2), trigonal planar (BF_3), tetrahedral (CH_4), pyramidal (NH_3), and bent (H_2O), showing how lone pairs progressively compress the bond angle



VSEPR Molecular Shapes

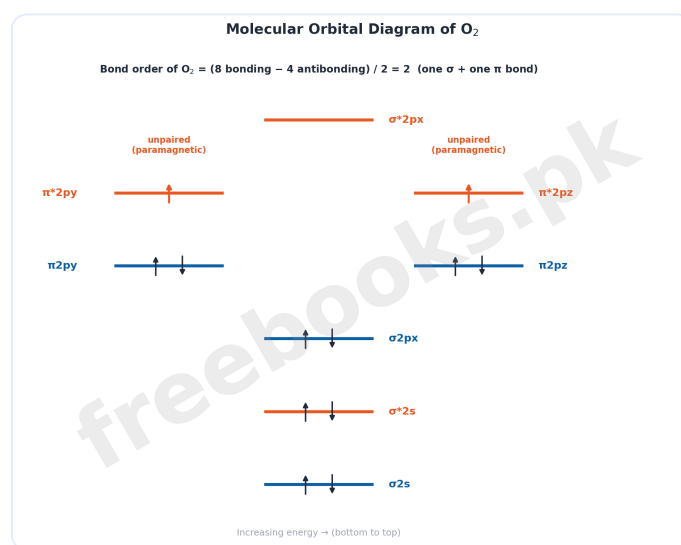
sp, sp², and sp³ Hybrid Orbital Geometries: Three panels showing the linear arrangement of sp orbitals in BeCl_2 , the trigonal planar arrangement of sp² orbitals in BF_3 , and the tetrahedral arrangement of sp³ orbitals in CH_4



sp, sp², and sp³ Hybrid Orbital Geometries



Molecular Orbital Diagram of Oxygen (O₂): An energy-level diagram showing bonding and antibonding molecular orbitals of O₂, with two unpaired electrons in the pi* orbitals responsible for its paramagnetism



Molecular Orbital Diagram of Oxygen (O₂)

Short Questions & Answers

Why does BF₃ have zero net dipole moment even though each B-F bond is polar?

BF₃ has a symmetric trigonal planar shape with three identical B-F bonds arranged 120 degrees apart; the individual bond dipole moments are equal in magnitude and point outward symmetrically, so their vector sum cancels exactly to zero, making the molecule nonpolar overall despite its polar bonds.

Why is CO₂ nonpolar while a bent triatomic molecule like SO₂ is polar?

CO₂ is linear, so its two identical, oppositely-directed C=O bond moments cancel exactly; SO₂ is bent, with a lone pair on sulfur, so its two S=O bond moments do not point in exactly opposite directions and their vector sum leaves a net dipole moment.

Why can period 2 elements not form expanded octets, while period 3 elements such as sulfur can?

Expanding an octet requires using empty d orbitals to hold the extra electron density, and period 2 elements have no d orbitals available in their valence shell, only 2s and 2p, while period 3 elements have accessible 3d orbitals that period 2 elements lack.



Why is the H-F bond energy much higher than H-I?

Bond energy rises with increasing electronegativity difference between the bonded atoms; fluorine is far more electronegative than iodine, so the H-F bond has greater polarity and additional electrostatic attraction that strengthens it well beyond the weaker, less polar H-I bond.

Why is ammonia's bond angle smaller than the ideal tetrahedral angle?

Ammonia's central nitrogen atom has one lone pair in addition to three bond pairs; because a lone pair occupies more space and repels more strongly than a bond pair, it compresses the three N-H bond pairs closer together, reducing the bond angle below the ideal tetrahedral value.

Why does water have an even smaller bond angle than ammonia?

Water's central oxygen atom has two lone pairs rather than one; with two space-occupying, strongly repelling lone pairs instead of one, the remaining two O-H bond pairs are compressed even further than in ammonia, giving a smaller bond angle.

How is the sp^3 hybridization of carbon in methane related to its bond geometry?

One 2s and three 2p orbitals of carbon mix to give four equivalent sp^3 hybrid orbitals arranged tetrahedrally at 109.5 degrees; each overlaps with a hydrogen 1s orbital to form a sigma bond, so the resulting molecule adopts the same tetrahedral shape as the hybrid orbitals themselves.

Why is the oxygen molecule paramagnetic according to molecular orbital theory?

The molecular orbital diagram of O_2 places one electron each, with parallel spins, into two separate antibonding pi-star orbitals rather than pairing them in one orbital; these two unpaired electrons give the molecule a net magnetic moment, making it paramagnetic and attracted into an external magnetic field.

Why does He_2 not exist, according to molecular orbital theory?

Combining the 1s orbitals of two helium atoms places two electrons in the bonding sigma orbital and two in the antibonding sigma-star orbital, giving a bond order of $(2-2)/2 = 0$; a bond order of zero means no net bonding, so the He_2 molecule simply does not form.

Why is the ionic bond in NaCl stronger than hydrogen bonding in water?



The ionic bond in NaCl has a bond energy of about 760 kJ/mol, arising from the strong electrostatic attraction between fully-charged Na^+ and Cl^- ions, while hydrogen bonding is a much weaker intermolecular force, only about 20-50 kJ/mol, arising from a comparatively weak dipole-type attraction rather than a full charge transfer.

Long Questions & Answers

Explain how Valence Bond Theory and orbital hybridization together account for the shapes and bonding of covalent molecules such as BeCl_2 , BF_3 , and CH_4 .

What does Valence Bond Theory say about how a covalent bond forms?

VBT states that a covalent bond forms when two half-filled atomic orbitals of similar energy, one from each atom, overlap along the axis joining their nuclei; greater orbital overlap produces a stronger bond, and the bond's direction is fixed by the shape and orientation of the overlapping orbitals.

What is the difference between a sigma bond and a pi bond?

A sigma bond forms by head-on, linear overlap of two orbitals along the internuclear axis and is present in every covalent bond; a pi bond forms by sideways overlap of two parallel p orbitals, giving electron density above and below the internuclear axis, and appears only in double and triple bonds alongside a sigma bond.

What is hybridization, and why is it needed to explain molecular shapes?

Hybridization is the mixing of atomic orbitals of comparable energy within a single atom into a new set of equivalent orbitals of the same energy and shape; it is needed because the shapes of pure, unmixed atomic orbitals, spherical s, dumbbell p, cannot by themselves account for the observed bond angles of real molecules.



How does sp hybridization explain the linear shape of BeCl₂?

Beryllium's one 2s and one 2p orbital mix to form two sp hybrid orbitals arranged at 180 degrees; each overlaps with a half-filled p orbital of a chlorine atom to form a sigma bond, so BeCl₂ adopts the same 180-degree linear arrangement as the hybrid orbitals themselves.

How do sp² and sp³ hybridization explain the shapes of BF₃ and CH₄?

In BF₃, boron's one 2s and two 2p orbitals mix to form three sp² orbitals arranged in a trigonal plane at 120 degrees, matching BF₃'s trigonal planar shape; in CH₄, carbon's one 2s and three 2p orbitals mix to form four sp³ orbitals arranged tetrahedrally at 109.5 degrees, matching methane's tetrahedral shape, with each hybrid orbital overlapping a hydrogen 1s orbital to form a sigma bond.

Describe the postulates of the VSEPR model and explain, using molecular orbital theory, why simple bonding theories fail to predict the paramagnetism of oxygen.

What are the key postulates of the VSEPR model?

Both lone pairs and bond pairs around a central atom determine molecular geometry; electron pairs arrange themselves as far apart as possible to minimize repulsion; lone pairs occupy more space and repel more strongly than bond pairs, so repulsion strength follows lone pair-lone pair greater than lone pair-bond pair greater than bond pair-bond pair; and a multiple bond, despite containing more than one electron pair, is treated as a single region of electron density.

How does the number of electron pairs around a central atom determine electron-pair geometry?

Two electron pairs give a linear geometry, three give trigonal planar, four give tetrahedral, five give trigonal bipyramidal, and six give octahedral; this electron-pair geometry is then adjusted for the molecule's actual shape by considering only the positions of the bonded atoms, excluding any lone pairs.



What are the postulates of molecular orbital theory?

Atomic orbitals of the combining atoms overlap to form new molecular orbitals belonging to the whole molecule; same-sign orbital overlap produces a lower-energy bonding orbital, while opposite-sign overlap produces a higher-energy antibonding orbital; and bond order, a measure of the number of bonds formed, equals half the difference between the number of electrons in bonding and antibonding orbitals.

What does the molecular orbital diagram of O₂ show about its electron arrangement?

Filling O₂'s molecular orbitals in order of increasing energy leaves two electrons to occupy the degenerate pi-star (2p_y) and pi-star (2p_z) antibonding orbitals; following Hund's rule, these two electrons occupy the two orbitals singly, with parallel spins, rather than pairing up in one.

Why can Valence Bond Theory not explain oxygen's paramagnetism, while molecular orbital theory can?

VBT depicts the oxygen-oxygen double bond simply as one sigma and one pi bond, formed from fully-paired shared electrons, and provides no way to represent unpaired electrons within that picture; MOT, by contrast, explicitly tracks how many electrons occupy each individual bonding and antibonding orbital, correctly revealing the two unpaired electrons in oxygen's antibonding pi-star orbitals that are directly responsible for its observed paramagnetism.

Multiple Choice Questions (MCQs)

A dative (coordinate covalent) bond differs from a normal covalent bond because:

- A. It involves ionic character
- B. Both shared electrons are donated by one atom only
- C. It is weaker than a normal covalent bond
- D. It only forms between identical atoms

Answer: B. Both shared electrons are donated by one atom only

Explanation: In a dative bond, one atom, the donor, supplies both electrons of



the shared pair, while in a normal covalent bond each atom contributes one electron.

The central sulfur atom in the sulfate ion, SO_4^{2-} , has how many electrons in its valence shell?

- A. 8
- B. 10
- C. 12
- D. 14

Answer: C. 12

Explanation: Calculating from its Lewis structure, sulfate's central S atom has 12 valence electrons, four more than a normal octet, an expanded octet made possible by its accessible 3d orbitals.

An electronegativity difference of 2.1 between two bonded atoms indicates:

- A. A nonpolar covalent bond
- B. A polar covalent bond
- C. An ionic bond
- D. No bond forms

Answer: C. An ionic bond

Explanation: An electronegativity difference above about 1.8 indicates an ionic bond, as seen in NaCl, which has a difference of 2.1.

CCl_4 has four individually polar C-Cl bonds but zero net dipole moment because:

- A. Carbon and chlorine have equal electronegativity
- B. Its tetrahedral symmetry causes the bond moments to cancel
- C. It has no lone pairs on carbon
- D. Chlorine atoms repel each other

Answer: B. Its tetrahedral symmetry causes the bond moments to cancel

Explanation: CCl_4 's perfectly tetrahedral, symmetric geometry causes the four equal C-Cl bond moments to cancel exactly, giving zero net dipole moment despite polar individual bonds.

Which bond type is generally the strongest, based on typical bond energies?



- A. London dispersion forces
- B. Hydrogen bonding
- C. Covalent bond
- D. Ionic bond

Answer: D. Ionic bond

Explanation: Ionic bonds, such as in NaCl at about 760 kJ/mol, are typically the strongest, well above covalent bonds, hydrogen bonds, and van der Waals forces.

A sigma bond is formed by:

- A. Sideways overlap of parallel p orbitals
- B. Head-on overlap of orbitals along the internuclear axis
- C. Overlap of only d orbitals
- D. Transfer of electrons between atoms

Answer: B. Head-on overlap of orbitals along the internuclear axis

Explanation: A sigma bond forms from head-on, linear overlap of two atomic orbitals along the axis joining the two nuclei.

Which hybridization explains the trigonal planar shape of BF₃?

- A. sp
- B. sp²
- C. sp³
- D. sp³d

Answer: B. sp²

Explanation: sp² hybridization mixes one s and two p orbitals into three orbitals arranged in a trigonal plane at 120 degrees, matching BF₃'s shape.

According to VSEPR theory, a central atom with 4 bond pairs and 2 lone pairs has a molecular shape that is:

- A. Tetrahedral
- B. Pyramidal
- C. Bent/V-shaped
- D. Linear

Answer: C. Bent/V-shaped

Explanation: Four electron pairs give a tetrahedral electron-pair geometry, but with 2 lone pairs excluded from the shape description, the actual molecular shape is bent or V-shaped, as in water.

The bond order of N₂, calculated from its molecular orbital diagram, is:



- A. 1
- B. 2
- C. 3
- D. 4

Answer: C. 3

Explanation: N₂ has 6 more bonding than antibonding valence electrons, giving a bond order of $(6-0)/2 = 3$, consistent with its triple bond.

Oxygen (O₂) is paramagnetic because its molecular orbital diagram shows:

- A. All electrons paired in bonding orbitals
- B. Two unpaired electrons in antibonding pi-star orbitals
- C. No electrons in antibonding orbitals
- D. A bond order of zero

Answer: B. Two unpaired electrons in antibonding pi-star orbitals

Explanation: O₂'s molecular orbital diagram places two electrons singly, with parallel spins, in separate antibonding pi-star orbitals, and these unpaired electrons cause its paramagnetism.

Quick Revision Summary

- Ionic bond: complete electron transfer, low-IE metal + high-EA nonmetal (e.g. NaCl)
- Covalent bond: mutual electron sharing; nonpolar if electronegativities equal, polar if different
- Dative (coordinate) bond: both shared electrons donated by one atom (e.g. H₃O⁺, CO, O₃)
- Expanded octet: central atom exceeds 8 valence electrons using d orbitals, period 3 or later only, e.g. SO₄²⁻, I₃⁻
- Electronegativity difference predicts bond type: below 0.4 nonpolar covalent | 0.4-1.8 polar covalent | above 1.8 ionic
- Dipole moment measures charge separation (Debye units); symmetric molecules (BeCl₂, BF₃, CCl₄) can have polar bonds but zero net dipole moment
- Bond energy rises with electronegativity difference and bond multiplicity; bond length rises with atom size, falls with electronegativity difference



- Bond strength order: ionic > covalent > hydrogen bonding > dipole-dipole > London dispersion
- VBT: sigma bond = head-on overlap; pi bond = sideways overlap of parallel p orbitals; double bond = 1 sigma + 1 pi; triple bond = 1 sigma + 2 pi
- Hybridization: sp = linear (180 degrees), sp² = trigonal planar (120 degrees), sp³ = tetrahedral (109.5 degrees)
- VSEPR: electron pairs arrange to minimize repulsion; lp-lp > lp-bp > bp-bp; lone pairs compress bond angles
- VSEPR shapes: 2 pairs = linear, 3 = trigonal planar, 4 = tetrahedral/pyramidal/bent, 5 = trigonal bipyramidal, 6 = octahedral
- MOT bond order = (bonding electrons - antibonding electrons) / 2; bond order 0 means no molecule (He₂)
- MOT explains O₂ paramagnetism, 2 unpaired electrons in pi* orbitals, something VBT cannot show

Exam Tips

- When predicting bond type, always compute the electronegativity difference first -- most 'ionic vs covalent' exam questions reduce to comparing this single number against 0.4 and 1.8
- For dipole moment questions, check symmetry before anything else: a molecule with identical ligands in a fully symmetric geometry (linear, trigonal planar, tetrahedral) always has zero net dipole moment even if every bond is polar
- Count electron pairs first, then look up the geometry, then subtract lone pairs for the actual shape -- this three-step VSEPR method avoids most shape-prediction errors
- Match hybridization to geometry directly: sp = linear, sp² = trigonal planar, sp³ = tetrahedral -- if you know one, you know the other
- For MOT bond-order questions, write out the molecular orbital filling order first (sigma2s, sigma*2s, then the 2p orbitals) before counting bonding vs antibonding electrons
- Remember that MOT, not VBT, is the theory that explains paramagnetism -- if a question asks why a substance is attracted to a magnet, look for unpaired electrons in antibonding orbitals



Chapter 4: Stoichiometry

Stoichiometry, from the Greek for 'measuring elements,' is the quantitative side of chemistry: given a balanced chemical equation, it lets you calculate exactly how much of each reactant is needed and how much of each product will form. Every calculation in this chapter rests on a single connecting idea, the mole, defined as the amount of substance containing as many elementary particles as there are atoms in exactly 12 grams of carbon-12, a number known as Avogadro's number, 6.02×10^{23} .

The mole links four otherwise very different quantities, mass (via molar mass), number of particles (via Avogadro's number), gas volume at STP (via molar volume, $22.4 \text{ dm}^3/\text{mol}$), and solution concentration (via molar concentration), so that any one of them can be converted into moles and then, using the ratios locked into a balanced equation, into the moles, and then the mass, volume, or concentration, of any other substance in the reaction. The chapter closes with three practical extensions of this idea: identifying the limiting reactant that caps how much product can form, comparing theoretical and actual yield through percentage yield, and recognizing why precise stoichiometric control is essential in the production and dosing of medicine.

Learning Objectives

- Derive measurements of mass, volume, and number of particles using moles
- State and use the volume of one mole of a gas at STP to solve mole-volume problems
- Calculate the molar mass of a gas from its density at STP
- Express balanced chemical equations in terms of moles, particles, masses, and gas volumes at STP
- Explain the concept of a limiting reagent and identify it from given reactant quantities
- Calculate the maximum amount of product and the amount of unreacted excess reagent
- Calculate theoretical yield, actual yield, and percentage yield



- Calculate the quantities of reactants and products involved in a reaction using stoichiometric principles
- Explain, with examples, the importance of stoichiometry in the production and dosage of medicine
- Perform mole-mole, mass-mass, volume-volume, mole-mass, mole-volume, and mass-volume stoichiometric conversions

Key Concepts

4.1 The Mole Concept and Molar Mass

A mole is the amount of substance containing as many elementary entities, atoms, molecules, ions, or other particles, as there are atoms in exactly 12 g of carbon-12; this number, Avogadro's number, is 6.02×10^{23} per mole. Chemists use the mole as their standard counting unit because atoms and molecules are far too small and numerous to count individually, but a mole of any substance always contains exactly this same number of particles, whatever the substance.

The molar mass of a substance, the mass of one mole expressed in grams, is numerically equal to its atomic, molecular, formula, or ionic mass and is found by summing the masses of its component atoms; for example, the molar mass of CCl_4 is $(1 \times 12.0) + (4 \times 35.5) = 154.0 \text{ g/mol}$. The number of moles in a given mass of a substance is then found from $n = m/M$, where m is the given mass and M is the molar mass -- for instance, 20 g of NaOH (molar mass 40 g/mol) is $20/40 = 0.5 \text{ mol}$.

4.2 Mole-Particle-Mass Relationships

Although one mole of any substance always contains the same number of particles, Avogadro's number, different substances need very different masses to reach that one mole, since the mole simply counts particles while mass reflects how heavy each individual particle is: 1.0 g of hydrogen, 23.0 g of sodium, and 238.0 g of uranium each contain exactly one mole, 6.02×10^{23} atoms, because a uranium atom is 238 times heavier than a hydrogen atom. The number of moles in a sample can equally be found from its particle count using $n = (\text{number of particles}) / N_A$, and this relationship applies identically to atoms, molecules, formula units, or ions -- one mole of SO_4^{2-} ions, for example,



contains 6.02×10^{23} ions, just as one mole of water contains 6.02×10^{23} molecules.

4.3 Molar Volume of Gases at STP

The molar volume is the volume occupied by one mole of any ideal gas at standard temperature and pressure (STP), and its value, 22.4 dm^3 , is the same for every gas regardless of its identity, a direct consequence of Avogadro's law that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. This gives a single powerful equivalence at STP: 22.4 dm^3 of any gas equals its molar mass in grams equals 6.02×10^{23} molecules equals one mole, so the volume of a gas sample at STP can be found directly from its number of moles using $V = n \times V_m$, and conversely the number of moles can be found from a known volume.

4.4 Molar Mass and Density of Gases

Since one mole of every ideal gas occupies the same volume at STP, a gas's density, its mass per unit volume, depends directly on its molar mass: gases with larger, heavier molecules are denser than gases with smaller, lighter ones at the same conditions. This relationship means that measuring the density of an unknown gas at STP is enough to calculate its molar mass, using $\text{molar mass} = \text{density} \times \text{molar volume}$; a gas with a density of 1.97 g/dm^3 at STP, for example, has a molar mass of $1.97 \times 22.4 = 44.1 \text{ g/mol}$.

4.5 Molar Concentration of Solutions

Molar concentration expresses how many moles of a dissolved substance are present per unit volume of solution, in units of mol/dm^3 , and is calculated as $C = n/V$, where n is the number of moles of solute and V is the volume of solution in dm^3 ; rearranged, this also gives $n = C \times V$, letting the number of moles in a solution of known concentration and volume be calculated directly. This relationship is essential for solution stoichiometry, since reactions in aqueous solution are far more commonly measured out by volume and concentration than by mass.



4.6 Stoichiometric Relationships from Balanced Equations

A balanced chemical equation encodes several equivalent relationships simultaneously: for $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, one can equally say that 1 mole of N_2 reacts with 3 moles of H_2 to form 2 moles of NH_3 , that 1 molecule reacts with 3 molecules to form 2 molecules, that 22.4 dm³ of N_2 reacts with 67.2 dm³ of H_2 to form 44.8 dm³ of NH_3 at STP, or that 28.0 g of N_2 reacts with 6.0 g of H_2 to form 34.0 g of NH_3 . Six distinct types of stoichiometric calculation follow from these relationships: mole-mole, mass-mass, volume-volume, mole-mass, mole-volume, and mass-volume, and all rest on the same three assumptions, that reactants convert completely to products, that mass is conserved, and that no side reactions occur.

Every stoichiometric calculation follows the same general path regardless of which quantities are given or asked for: first, convert the known quantity, mass, gas volume, or solution concentration, of a known substance into moles using the relevant formula ($n = m/M$, $n = V/V_m$, or $n = CV$); second, use the mole ratio from the balanced equation to find the moles of the unknown substance; and third, convert those moles of the unknown back into whatever quantity, mass, volume, or concentration, the question asks for.

4.7 Limiting and Excess Reactants

Reactants in a real reaction mixture are rarely present in the exact ratio given by the balanced equation; the reactant that is completely consumed first is called the limiting reactant, and it determines the maximum amount of product that can form, since the reaction simply stops once the limiting reactant runs out, regardless of how much of the other reactant, the excess reactant, remains. Excess reactant is often deliberately supplied in large amounts to ensure that a more expensive or reaction-critical reactant is fully converted, to maximize product yield, or to speed up the reaction.

The limiting reactant is identified by calculating, from the moles of each reactant actually available, how much product each one alone could theoretically produce using the balanced equation's mole ratios; whichever reactant yields the smaller amount of product is the limiting reactant, since it will run out first and cap the reaction at that lower amount. Once the limiting reactant is identified, the same



mole ratio can be used in reverse to calculate exactly how much of the excess reactant was actually consumed, and subtracting this from the amount originally supplied gives the mass of excess reactant left over.

4.8 Theoretical Yield, Actual Yield, and Percentage Yield

Theoretical yield is the maximum amount of product a reaction can produce, calculated directly from the balanced equation and the amount of limiting reactant, while actual yield is the amount of product actually recovered in practice, and it is almost always smaller because of incomplete reactions, competing side reactions, reversible reactions running backward, or losses during purification steps like filtration, distillation, or crystallization. The efficiency of a reaction is expressed as its percentage yield, calculated as (actual yield / theoretical yield) x 100, with a higher percentage yield indicating a more efficient reaction.

4.9 Importance of Stoichiometry in Medicine

Precise stoichiometric control is essential throughout the production and dosing of medicine, since a drug typically has no therapeutic effect when under-dosed but can become toxic or fatal when over-dosed. Stoichiometric principles ensure that antibiotic doses match their target bacteria, allow accurate measurement of cholesterol and blood glucose levels for diagnosis and insulin dosing, are used in doping tests to detect steroids and stimulants in athletes' urine, ensure vaccines contain the correct concentration of viral antigen, and guarantee that medicines such as paracetamol are dosed accurately, since an overdose can cause severe, even fatal, organ damage.

Important Definitions

What is a mole?

The amount of substance containing 6.02×10^{23} (Avogadro's number) elementary entities, the same number of atoms as in 12 g of carbon-12.

What is molar mass?

The mass of one mole of a substance, expressed in g/mol, numerically equal to its atomic, molecular, or formula mass.



What is Avogadro's number?

The number of elementary entities contained in one mole of any substance, equal to 6.02×10^{23} per mole.

What is molar volume?

The volume occupied by one mole of any ideal gas at STP, equal to 22.4 dm³.

What is molar concentration?

The number of moles of solute dissolved per dm³ of solution, expressed in mol/dm³.

What is a limiting reactant?

The reactant that is completely consumed first in a reaction, capping the maximum amount of product that can form.

What is an excess reactant?

The reactant that remains partially unreacted once the limiting reactant has been fully used up.

What is theoretical yield?

The maximum amount of product calculable from the balanced equation and the amount of limiting reactant available.

What is actual yield?

The amount of product actually obtained when a reaction is carried out in practice.

What is percentage yield?

Actual yield divided by theoretical yield, multiplied by 100, expressing how efficiently a reaction converts reactants into product.

Key Facts and Relations

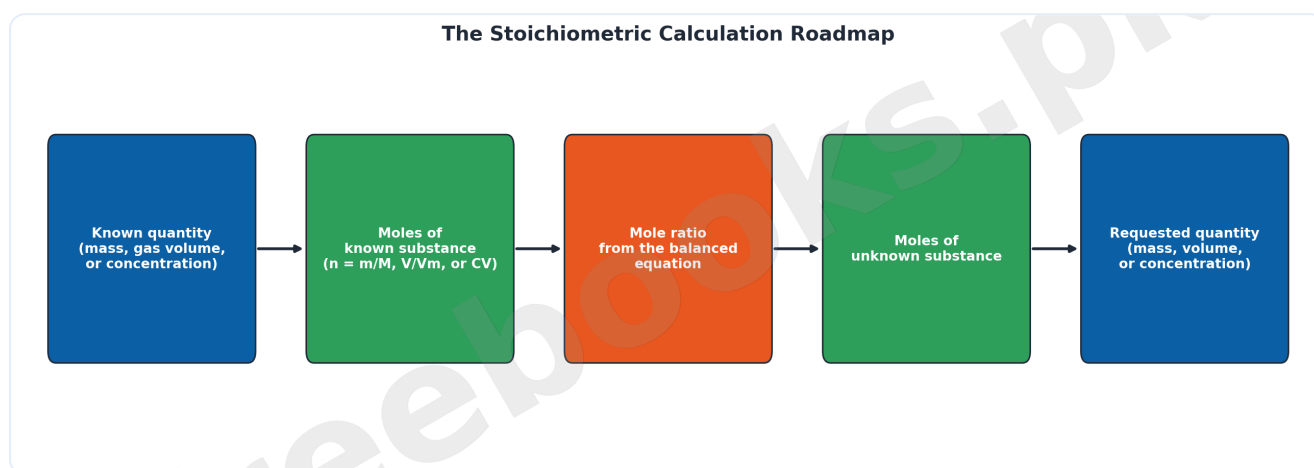
Topic	Key Fact / Relation
Number of moles from mass	$n = m / M$
Mass from number of moles	$m = n \times M$



Topic	Key Fact / Relation
Number of moles from particle count	$n = N / N_A$ ($N_A = 6.02 \times 10^{23} / \text{mol}$)
Molar volume at STP	$V_m = 22.4 \text{ dm}^3/\text{mol}$
Volume of a gas at STP	$V = n \times V_m$
Molar mass from gas density	Molar mass = density $\times V_m$
Molar concentration	$C = n / V$, so $n = C \times V$
Percentage yield	% Yield = (Actual yield / Theoretical yield) $\times 100$
STP equivalence	22.4 dm ³ of any gas = its molar mass in g = 6.02×10^{23} molecules = 1 mole
Limiting reactant rule	The reactant that produces the LEAST amount of product, by calculation, is the limiting reactant

Diagrams

The Stoichiometric Calculation Roadmap: A flowchart showing the standard path for any stoichiometry problem: a known mass, gas volume, or concentration is converted to moles, then to moles of the unknown substance using the balanced equation's mole ratio, then converted to the requested mass, volume, or concentration



The Stoichiometric Calculation Roadmap

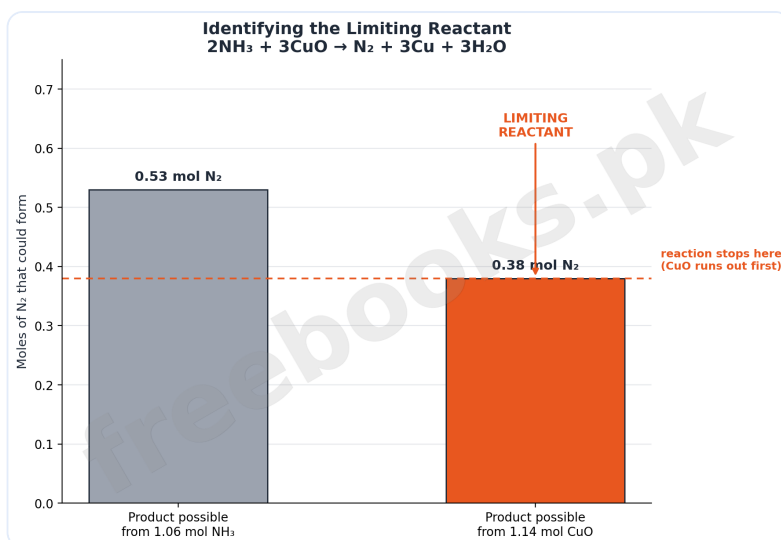


The Mole as a Central Hub: A hub-and-spoke diagram showing how the mole connects mass (via molar mass), number of particles (via Avogadro's number), gas volume at STP (via molar volume), and solution concentration (via $C = n/V$)



The Mole as a Central Hub

Identifying the Limiting Reactant: A bar comparison showing how much product two different reactants in the reaction $2\text{NH}_3 + 3\text{CuO} \rightarrow \text{N}_2 + 3\text{Cu} + 3\text{H}_2\text{O}$ could each produce if they reacted completely, with the smaller value identifying CuO as the limiting reactant and the reaction stopping there



Identifying the Limiting Reactant



Short Questions & Answers

Why do 1.0 g of hydrogen and 23.0 g of sodium both contain the same number of atoms?

Both quantities represent exactly one mole, and one mole of any element always contains Avogadro's number of atoms, 6.02×10^{23} ; sodium simply requires 23 times more mass than hydrogen to reach one mole, because a single sodium atom is 23 times heavier than a single hydrogen atom.

Why do 4 g of helium, 17 g of ammonia, and 64 g of sulfur dioxide all occupy 22.4 dm³ at STP, despite having very different molecular masses?

According to Avogadro's law, equal volumes of gases at the same temperature and pressure contain equal numbers of molecules, regardless of what the gas is; since each of these masses represents exactly one mole of its respective gas, each one contains Avogadro's number of molecules and therefore occupies the same molar volume, 22.4 dm³, at STP.

How can the molar mass of an unknown gas be found from its density at STP?

Since one mole of any gas occupies 22.4 dm³ at STP, multiplying the gas's density, mass per dm³, by the molar volume, 22.4 dm³/mol, gives the mass of one mole directly, which is the molar mass.

What is the difference between a limiting reactant and an excess reactant?

The limiting reactant is completely consumed first and therefore determines the maximum amount of product that can form; the excess reactant is supplied in a greater amount than stoichiometrically required and has some quantity left unreacted once the limiting reactant runs out.

Why is excess reactant often deliberately used in industrial reactions?

Supplying a large, often inexpensive, excess of one reactant helps ensure that a more expensive or critical reactant is converted as completely as possible, maximizes the amount of product formed, and can also increase the rate of reaction.



How is the limiting reactant identified when given the masses of two reactants?

Convert each reactant's mass to moles, then use the balanced equation's mole ratios to calculate how much product each reactant could produce on its own if it reacted completely; the reactant that yields the smaller amount of product is the limiting reactant, since it runs out first.

Why is the actual yield of a reaction usually less than its theoretical yield?

Actual yield falls short of theoretical yield because of losses during purification steps like filtration or crystallization, because some reactant may be diverted into a competing side reaction, or because a reversible reaction runs partly backward, reducing the net amount of product formed.

How is percentage yield calculated, and what does a higher value indicate?

Percentage yield equals actual yield divided by theoretical yield, multiplied by 100; a higher percentage yield indicates a more efficient reaction, with less product lost to side reactions, incomplete conversion, or purification losses.

Why is precise stoichiometry critical when dosing a medicine like paracetamol?

A medicine typically has no therapeutic effect if under-dosed, but can become toxic, causing effects such as severe liver damage, if over-dosed; stoichiometric calculations ensure that each dose contains precisely the amount of active ingredient needed to be both effective and safe.

Why does 22.4 dm³ of CO₂ at STP have the same number of molecules as 22.4 dm³ of H₂ at STP, despite CO₂ being a much heavier molecule?

Avogadro's law states that equal volumes of any gas at the same temperature and pressure contain equal numbers of molecules, regardless of the individual molecule's mass or size; molar volume depends only on the number of gas particles present, not on their identity or mass.



Long Questions & Answers

Describe the mole concept and explain how it connects mass, number of particles, and gas volume, using worked relationships.

What is the mole, and why do chemists use it?

A mole is the amount of substance containing as many elementary entities as there are atoms in exactly 12 g of carbon-12, a fixed number known as Avogadro's number, 6.02×10^{23} . Chemists use it because atoms and molecules are too small and numerous to count directly, and the mole provides a convenient, universal counting unit that works identically for atoms, molecules, ions, or any other particle.

How is the number of moles calculated from a given mass?

The number of moles is found using $n = m/M$, where m is the given mass of the substance and M is its molar mass in g/mol; for example, 20 g of NaOH, with a molar mass of 40 g/mol, contains $20/40 = 0.5$ mol.

How is the number of moles related to the number of particles?

The number of moles equals the number of particles divided by Avogadro's number, $n = N/N_A$; this relationship holds for atoms, molecules, formula units, or ions alike, since one mole of any of these always contains exactly 6.02×10^{23} particles.

How is the number of moles of a gas related to its volume at STP?

At standard temperature and pressure, one mole of any ideal gas occupies 22.4 dm³, the molar volume; the volume of a gas sample is therefore found using $V = n \times V_m$, and conversely the number of moles can be calculated from a measured volume by dividing by 22.4 dm³/mol.

How can molar mass be determined from a gas's density at STP?

Since density is mass per unit volume, and one mole of any gas occupies the same 22.4 dm³ at STP, multiplying a gas's density at STP by the molar volume



gives the mass of exactly one mole, which is its molar mass: $\text{molar mass} = \text{density} \times 22.4 \text{ dm}^3/\text{mol}$.

Explain how to identify the limiting reactant in a reaction and how to calculate the theoretical, actual, and percentage yield of a reaction.

What is a limiting reactant, and why does it control the amount of product formed?

The limiting reactant is the reactant that is completely consumed first during a reaction; because a reaction stops once any one reactant runs out, the amount of product that can form is capped by however much of that limiting reactant was available, regardless of how much of the other, excess, reactant remains.

What steps are used to identify the limiting reactant from given reactant quantities?

First, convert the given mass, or volume, or concentration and volume, of each reactant into moles. Second, use the balanced equation's mole ratios to calculate how many moles of product each reactant could produce on its own, assuming it reacted completely. Third, compare these values: the reactant that yields the smaller amount of product is the limiting reactant.

How is the mass of excess reactant remaining after a reaction calculated?

Once the limiting reactant is identified, its mole ratio with the excess reactant, from the balanced equation, is used to calculate how many moles of the excess reactant were actually consumed during the reaction; subtracting this consumed amount from the excess reactant's original number of moles, then converting to mass, gives the mass of excess reactant left over.

What is the difference between theoretical yield and actual yield?

Theoretical yield is the maximum amount of product that calculation from the balanced equation and the limiting reactant predicts should form; actual yield is the amount of product actually recovered when the reaction is carried out in the laboratory or industrially, and is almost always somewhat lower due to side reactions, reversibility, or purification losses.



How is percentage yield calculated, and why is it a useful measure?

Percentage yield is calculated as actual yield divided by theoretical yield, multiplied by 100; it is useful because it expresses, as a single comparable number, how efficiently a reaction converts its reactants into the desired product, letting chemists compare the efficiency of different reaction conditions or procedures.

Multiple Choice Questions (MCQs)

Which of the following statements about one mole of ozone gas, O₃, is correct?

- A. It contains Avogadro's number of O₃ molecules
- B. It contains half of Avogadro's number of O₃ molecules
- C. It contains twice Avogadro's number of O₃ molecules
- D. It contains no fixed number of molecules

Answer: A. It contains Avogadro's number of O₃ molecules

Explanation: One mole of any substance, including ozone gas, always contains exactly Avogadro's number, 6.02×10^{23} , of its formula unit, in this case O₃ molecules.

Which of the following samples has the greatest mass? (molar masses: N₂ = 28, NH₃ = 17, He = 4, CO₂ = 44 g/mol)

- A. 0.5 mol of N₂
- B. 0.5 mol of NH₃
- C. 0.5 mol of He
- D. 0.5 mol of CO₂

Answer: D. 0.5 mol of CO₂

Explanation: Mass = moles $\times$ molar mass; with equal moles, 0.5 mol, the sample with the highest molar mass, CO₂ at 44 g/mol, has the greatest mass, 22 g.

Which of the following gas samples has the greatest volume at STP? (molar masses: CO₂ = 44, N₂O = 44, CO = 28, N₂ = 28 g/mol)

- A. 22 g of CO₂
- B. 88 g of N₂O
- C. 28 g of CO



D. 28 g of N₂

Answer: B. 88 g of N₂O

Explanation: Converting each to moles: 22 g CO₂ = 0.5 mol, 88 g N₂O = 2.0 mol, 28 g CO = 1.0 mol, 28 g N₂ = 1.0 mol; since volume at STP is proportional to moles, 88 g of N₂O, 2.0 mol, has the greatest volume.

A container holds 0.5 moles of an ideal gas at STP. What is its volume?

A. 11.2 dm³

B. 22.4 dm³

C. 44.8 dm³

D. 12.2 dm³

Answer: A. 11.2 dm³

Explanation: $V = n \times V_m = 0.5 \text{ mol} \times 22.4 \text{ dm}^3/\text{mol} = 11.2 \text{ dm}^3$.

A solution contains 4.0 g of NaOH, molar mass 40 g/mol, in 250 cm³ of solution. What is its molar concentration?

A. 0.10 mol/dm³

B. 0.20 mol/dm³

C. 0.40 mol/dm³

D. 0.80 mol/dm³

Answer: C. 0.40 mol/dm³

Explanation: Moles of NaOH = $4.0/40 = 0.1 \text{ mol}$; volume = 0.250 dm³; $C = n/V = 0.1/0.250 = 0.40 \text{ mol/dm}^3$.

A gas has a density of 1.43 g/dm³ at STP. What is its molar mass?

A. 14.3 g/mol

B. 22.4 g/mol

C. 32.0 g/mol

D. 64.0 g/mol

Answer: C. 32.0 g/mol

Explanation: Molar mass = density $\times$ molar volume = $1.43 \text{ g/dm}^3 \times 22.4 \text{ dm}^3/\text{mol} = 32.0 \text{ g/mol}$.

In the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, if 2 moles of N₂ and 3 moles of H₂ are mixed, which reactant is limiting?

A. N₂

B. H₂

C. Neither, they react completely



D. Cannot be determined

Answer: B. H₂

Explanation: 2 mol N₂ would require 6 mol H₂ to react completely, but only 3 mol H₂ is available; H₂ therefore runs out first and is the limiting reactant.

Which of the following best describes the theoretical yield of a reaction?

- A. The amount of product actually recovered in the lab
- B. The maximum amount of product calculated from the balanced equation
- C. The amount of excess reactant remaining
- D. The percentage efficiency of the reaction

Answer: B. The maximum amount of product calculated from the balanced equation

Explanation: Theoretical yield is the maximum amount of product predicted by stoichiometric calculation from the balanced equation and the limiting reactant, before accounting for real-world losses.

A reaction has a theoretical yield of 10.0 g and an actual yield of 7.5 g. What is the percentage yield?

- A. 25%
- B. 75%
- C. 1.33%
- D. 133%

Answer: B. 75%

Explanation: Percentage yield = (actual/theoretical) x 100 = (7.5/10.0) x 100 = 75%.

Why is stoichiometric precision especially critical in drug dosage, such as with paracetamol?

- A. Because drugs are always more effective in larger doses
- B. Because an underdose or overdose can be ineffective or dangerously toxic
- C. Because stoichiometry only applies to solid drugs
- D. Because drug reactions do not follow the law of conservation of mass

Answer: B. Because an underdose or overdose can be ineffective or dangerously toxic

Explanation: A medicine typically produces no therapeutic effect if underdosed



but can be toxic or even fatal if overdosed, making precise stoichiometric control of the active ingredient essential.

Quick Revision Summary

- Mole = amount of substance containing Avogadro's number, 6.02×10^{23} , of elementary entities
- Molar mass (M) = mass of 1 mole in g/mol; $n = m/M$
- $n = N/N_A$ relates moles to number of particles
- Molar volume (V_m) = 22.4 dm³/mol for any ideal gas at STP (Avogadro's law);
 $V = n \times V_m$
- Molar mass from gas density: molar mass = density $\times V_m$
- Molar concentration: $C = n/V$ (mol/dm³); $n = C \times V$
- STP equivalence: 22.4 dm³ of any gas = molar mass in g = 6.02×10^{23} molecules = 1 mole
- Stoichiometric calculation path: known quantity $\rightarrow$ moles $\rightarrow$ mole ratio from equation $\rightarrow$ moles of unknown $\rightarrow$ requested quantity
- 6 types of stoichiometric relationships: mole-mole, mass-mass, volume-volume, mole-mass, mole-volume, mass-volume
- Limiting reactant: consumed first, caps maximum product; excess reactant: remains unreacted
- Identify limiting reactant by comparing product yield calculated from each reactant separately; smaller value wins
- Theoretical yield = maximum product from calculation; actual yield = product actually obtained (usually less)
- % Yield = (actual yield / theoretical yield) $\times$ 100
- Stoichiometry is essential in medicine: dosing accuracy, antibiotic potency, blood glucose/cholesterol testing, vaccine antigen concentration

Exam Tips

- Always convert every given quantity to moles FIRST, no matter what units the question gives, mass, volume, concentration, or particle count -- moles are the universal bridge between all stoichiometric quantities



- For limiting reactant problems, never assume the reactant with the smaller mass or fewer moles is automatically limiting -- always calculate how much product each reactant would produce and compare
- Remember molar volume, $22.4 \text{ dm}^3/\text{mol}$, applies ONLY at STP -- don't use it for gas volumes at other temperatures or pressures
- For percentage yield questions, always calculate theoretical yield using the limiting reactant, never the excess reactant
- Keep track of units carefully throughout multi-step conversions, g, mol, dm^3 , mol/dm^3 -- most stoichiometry errors come from dropped or mismatched units, not wrong formulas
- Practice the standard roadmap, quantity $\rightarrow$ moles $\rightarrow$ mole ratio $\rightarrow$ moles of unknown $\rightarrow$ requested quantity, until it becomes automatic; nearly every numerical question in this chapter follows this same shape



Chapter 5: States and Phases of Matter

Matter exists in four states, solid, liquid, gas, and plasma, and the physical differences between them come down to a single variable: how strongly the particles inside attract one another and how much freedom they have to move. Gases have negligible intermolecular forces and expand to fill any container; the ideal gas equation, $PV = nRT$, captures how their pressure, volume, temperature, and amount are related, and can even be rearranged to calculate a gas's relative molecular mass from measurable quantities.

Liquids and solids, by contrast, are held together by intermolecular forces whose strength directly explains everyday behavior: London dispersion forces, permanent dipole-dipole forces, and hydrogen bonding together determine a substance's boiling point, viscosity, and surface tension, and hydrogen bonding in particular gives water its unusual, life-sustaining properties, from ice floating on water to its unusually high boiling point. The chapter closes by comparing crystalline and amorphous solids, and introducing liquid crystals, a state of matter between liquid and solid that underlies technologies from LCD screens to medical diagnostics.

Learning Objectives

- Describe the physical properties of gases, including compressibility, expandability, and pressure exerted by gases
- Describe the origin of gas pressure in terms of molecular collisions with the container walls
- State and use the ideal gas equation, $PV = nRT$, in calculations including the determination of relative molecular mass
- Describe simple properties of liquids using kinetic molecular theory
- Describe the three types of intermolecular forces and explain the strength and applications of dipole-dipole forces, hydrogen bonding, and London forces
- Describe physical properties of liquids such as evaporation, vapour pressure, boiling point, viscosity, and surface tension



- Apply the concept of hydrogen bonding to explain the unique properties of water
- Define molar heat of fusion and molar heat of vaporization, and describe their effect on matter particles
- Describe liquid crystals, their properties, and their uses in daily life
- Differentiate between amorphous and crystalline solids, and describe the properties of crystalline solids

Key Concepts

5.1 Properties of Gases and the Ideal Gas Equation

Gases have no definite shape or volume, expanding to fill whatever container holds them, because their molecules are widely separated, occupying only about 0.1% of the total volume, with the rest being empty space; this is why gases can be compressed so easily, and why sudden expansion of a gas causes cooling, an effect known as the Joule-Thomson effect. Gas pressure arises entirely from the collisions of gas molecules with the walls of their container, and in an ideal gas, intermolecular forces and particle volume are both taken as negligible.

Combining Boyle's law, V proportional to $1/P$, Charles's law, V proportional to T , and Avogadro's law, V proportional to n , gives the ideal gas equation, $PV = nRT$, where R , the ideal gas constant, equals $0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$. Substituting $n = m/M$ into this equation and rearranging gives $M = mRT/PV$, allowing the relative molecular mass of an unknown gas to be calculated directly from its measured mass, pressure, volume, and temperature.

5.2 Properties of Liquids and Intermolecular Forces

Liquids diffuse, like gases, but far more slowly, since their molecules are held closer together by comparatively strong intermolecular forces; they are about 100,000 times less compressible than gases but about 10 times more compressible than solids, and their molecules remain in constant, though slower, random motion, which is why liquids can flow and mix by diffusion. Three types of intermolecular force act between liquid molecules: instantaneous dipole-induced dipole forces, also called London dispersion forces, permanent dipole-permanent dipole forces, and hydrogen bonding.



London dispersion forces arise when the moving electrons of one molecule momentarily create an instantaneous dipole, which induces a temporary dipole in a neighboring molecule, producing a brief mutual attraction; these are the only intermolecular forces present between nonpolar molecules, and they strengthen with increasing molecular mass and size, as seen going down the halogen and noble gas families, and with increasing molecular surface area, as seen comparing straight-chain and branched isomers of pentane. Permanent dipole-permanent dipole forces, by contrast, arise when the positive end of one polar molecule is attracted to the negative end of a neighboring polar molecule, as between HCl or chloroform molecules.

5.3 Hydrogen Bonding

Hydrogen bonding is a special, unusually strong type of dipole-dipole force, weaker than covalent, ionic, or metallic bonds but stronger than any other intermolecular force; it forms when a hydrogen atom covalently bonded to a small, highly electronegative atom, F, O, or N, is attracted to a lone pair on a nearby electronegative atom of the same kind. The number of hydrogen bonds a molecule can form on average depends on both the number of hydrogen atoms bonded to F, O, or N and the number of available lone pairs; water, with two hydrogen atoms and two lone pairs on oxygen, forms an average of two hydrogen bonds per molecule and is extensively hydrogen bonded in three dimensions, while ammonia, despite having three hydrogen atoms, has only one lone pair on nitrogen and so can form only one hydrogen bond, giving it a much lower boiling point, -33 degrees C, than water, 100 degrees C.

5.4 Hydrogen Bonding and the Anomalous Properties of Water

Water's extensive three-dimensional hydrogen bonding gives it a set of unusual properties essential to life. When water freezes, its molecules arrange into a regular, extensively hydrogen-bonded tetrahedral lattice that contains more empty space than liquid water, so ice occupies about 9% more volume and is less dense than liquid water, causing ice to float; this insulates the water beneath frozen lakes and oceans, letting aquatic life survive winter. Water's strong hydrogen bonding also gives it an unusually high specific heat capacity, 4.18 J/g degrees C, letting it absorb or release large amounts of heat with only small temperature changes.



Water's molar heat of vaporization, 40.6 kJ/mol, is the highest among the group 16 hydrides, breaking the trend of steadily increasing heat of vaporization from H_2S to H_2Po that would otherwise be expected from London dispersion forces alone, because its extensive hydrogen bonding makes its molecules unusually difficult to separate; this same hydrogen bonding gives water its remarkably high boiling point relative to the other group 16 hydrides. Hydrogen bonding is also responsible for water's high surface tension, from the strong inward pull of hydrogen-bonded surface molecules, and its comparatively high viscosity, which exceeds that of many hydrocarbons and alcohols whose molecules form fewer or no hydrogen bonds.

5.5 Surface Tension and Viscosity of Liquids

Surface tension is the downward, inward pull exerted on molecules at a liquid's surface by the molecules beneath it, arising from unbalanced intermolecular attraction and causing the liquid surface to behave like a stretched skin that tends to minimize its area, which is why droplets form spheres; surface tension decreases as temperature rises and increases with stronger intermolecular forces. Viscosity, a liquid's resistance to flow, similarly rises with stronger intermolecular forces, since strongly attracted molecules cannot move past one another as freely, and falls as temperature rises, since molecules gain enough kinetic energy to overcome their attractive forces more easily.

5.6 Evaporation, Vapour Pressure, and Boiling Point

Evaporation is the spontaneous escape of high-energy molecules from a liquid's surface into the vapour phase at any temperature; because only the highest-energy molecules escape, the average kinetic energy, and therefore the temperature, of the remaining liquid falls, which is why evaporation causes cooling, as felt after a bath or from water kept in a porous earthenware vessel. In a closed container, escaped vapour molecules can also return to the liquid by condensation, and once the rate of evaporation equals the rate of condensation, a dynamic equilibrium is reached; the pressure exerted by the vapour at this equilibrium is called the vapour pressure, which rises with temperature and is lower for liquids with stronger intermolecular forces.



A liquid boils once its vapour pressure becomes equal to the external, atmospheric, pressure, allowing bubbles of vapour to form throughout the liquid and escape at the surface; boiling point therefore rises with stronger intermolecular forces, which lower vapour pressure at a given temperature, and with higher external pressure, since more heat is then needed to raise the vapour pressure to match it, which is why water boils at a lower temperature on a high mountain and at a higher temperature inside a sealed pressure cooker.

5.7 Energetics of Phase Changes

The molar heat of fusion is the heat absorbed by one mole of a solid to melt into liquid at its melting point, and the molar heat of vaporization is the heat absorbed by one mole of a liquid to become vapour at its boiling point; both quantities rise with stronger intermolecular forces, since more energy is needed to separate more strongly attracted particles, which is why water's heat of vaporization, 40.6 kJ/mol, far exceeds that of ammonia, 21.7 kJ/mol, or hydrogen chloride, 15.6 kJ/mol. Water's unusually high heat of fusion, 4.6 kJ/mol, is central to the stability of glaciers, ice sheets, and polar ice caps, since it means a large amount of energy is needed to melt ice, and it plays an important role in moderating sea level and reflecting sunlight to help regulate Earth's temperature.

5.8 Properties of Solids and Types of Solids

Solids are rigid substances with definite shape and volume, whose closely packed particles are held in place by strong ionic, covalent, metallic, or van der Waals forces; because these particles can only vibrate about fixed mean positions rather than move or rotate freely, solids resist compression and expand very little on heating compared to liquids and gases, and their only form of kinetic energy is vibrational. Solids are classified as either crystalline, with a definite, regular, three-dimensional geometric arrangement of particles, such as diamond, sodium chloride, and ice, or amorphous, lacking any such long-range order, such as glass, wood, and charcoal.

Crystalline solids share several distinctive properties: a definite geometrical shape with constant interfacial angles, sharp, well-defined melting points, characteristic cleavage planes along which they break, and a specific habit, the



shape in which a crystal characteristically grows under given conditions, that can change if growth conditions are altered. Amorphous solids, by contrast, melt gradually over a range of temperatures rather than sharply, can be molded and blown into different shapes, and are isotropic, meaning their properties are the same in every direction, unlike the anisotropic, direction-dependent properties of crystalline solids.

5.9 Liquid Crystals

Liquid crystals are substances that, over a certain temperature range, exist in a phase between fully liquid and fully solid: their typically rigid, rod-like molecules can migrate through the fluid and spin around their long axis like a liquid, yet remain roughly parallel to one another and cannot rotate end over end, giving them some of the ordered, anisotropic optical properties of a crystalline solid. This unusual combination of properties makes liquid crystals useful in electro-optic devices that control light, most familiarly in liquid crystal displays used in televisions, computers, and mobile phones, and also in diagnostic devices that detect tumors by their characteristically higher temperature and in temperature sensors that identify faulty circuit connections.

Important Definitions

What is the ideal gas constant, R ?

The proportionality constant in the ideal gas equation, $PV = nRT$, equal to $0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$.

What is a London dispersion force?

A weak, momentary force of attraction between an instantaneous dipole in one molecule and an induced dipole in a neighboring molecule.

What is a permanent dipole-dipole force?

The force of attraction between the positive end of one polar molecule and the negative end of a neighboring polar molecule.

What is a hydrogen bond?

A strong dipole-dipole attraction between a hydrogen atom bonded to F, O, or N and a lone pair on a nearby F, O, or N atom.

What is vapour pressure?



The pressure exerted by a liquid's vapour when it is in dynamic equilibrium with its liquid at a given temperature.

What is boiling point?

The temperature at which a liquid's vapour pressure becomes equal to the external, atmospheric, pressure.

What is molar heat of fusion?

The heat absorbed by one mole of a solid to melt into liquid at its melting point at 1 atmosphere pressure.

What is molar heat of vaporization?

The heat absorbed by one mole of a liquid to convert into vapour at its boiling point at 1 atmosphere pressure.

What is a crystal lattice?

The regular, repeating three-dimensional arrangement of ions, atoms, or molecules in a crystalline solid.

What is a liquid crystal?

A substance existing in a phase between liquid and solid, with molecules that flow like a liquid but retain some ordered, crystal-like orientation.

Key Facts and Relations

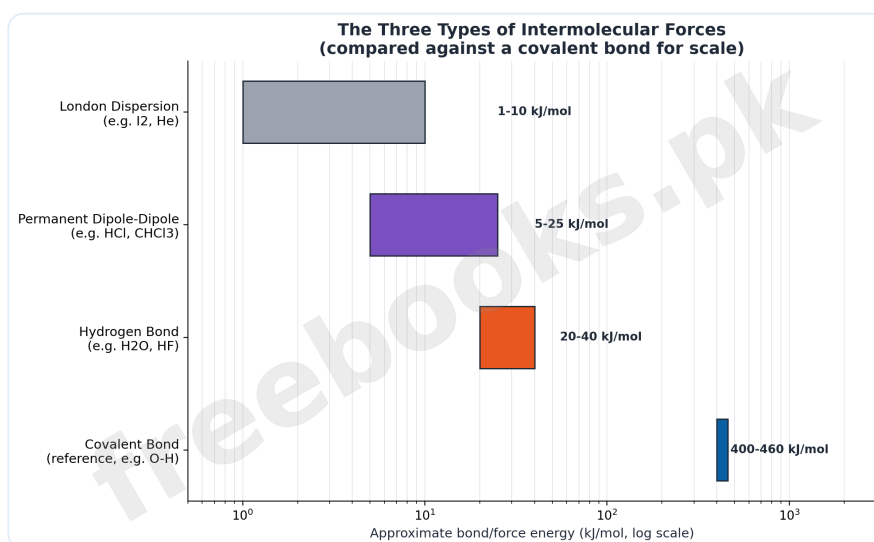
Topic	Key Fact / Relation
Ideal gas equation	$PV = nRT$
Ideal gas constant	$R = 0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$
Relative molecular mass from gas data	$M = mRT / PV$
Boyle's law	V is proportional to $1/P$ (n, T constant)
Charles's law	V is proportional to T (n, P constant)
Avogadro's law	V is proportional to n (P, T constant)
Molar heat of fusion of water	$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$, $\Delta H_f = 4.6 \text{ kJ/mol}$



Topic	Key Fact / Relation
Molar heat of vaporization of water	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$, $\Delta H_v = 40.6 \text{ kJ/mol}$
Specific heat capacity of water	$4.18 \text{ J/g degrees C}$
Ice expansion on freezing	Ice occupies about 9% more volume than the liquid water it forms from

Diagrams

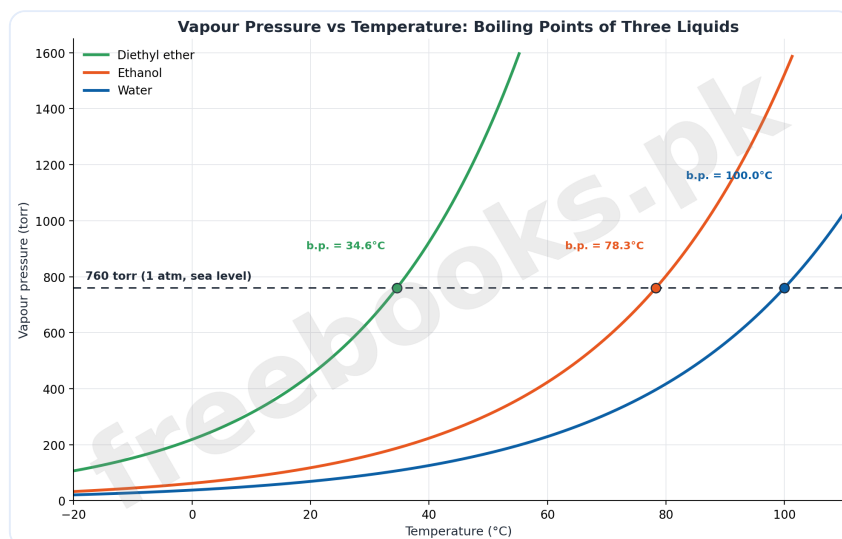
The Three Types of Intermolecular Forces: A comparison of London dispersion forces, permanent dipole-dipole forces, and hydrogen bonding by approximate strength, shown against a covalent bond for scale



The Three Types of Intermolecular Forces

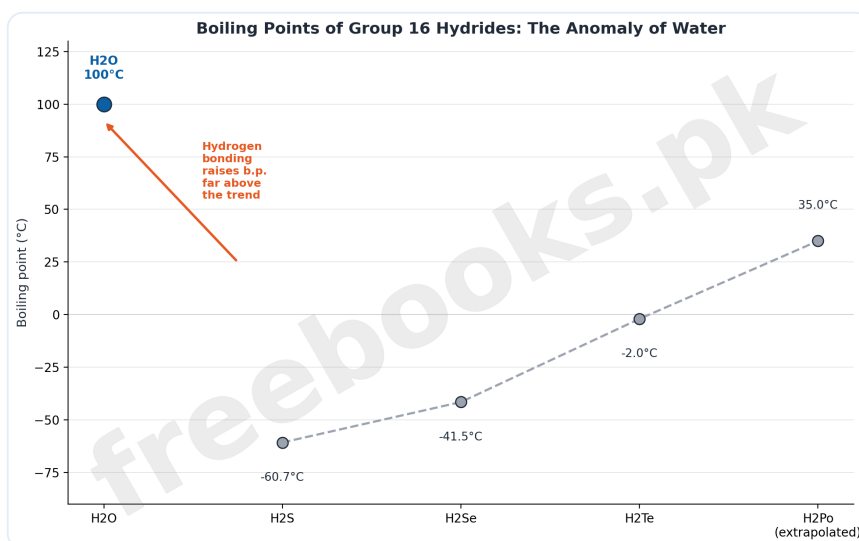
Vapour Pressure vs Temperature: Boiling Points of Three Liquids: A graph of vapour pressure against temperature for diethyl ether, ethanol, and water, showing each liquid's boiling point as the temperature where its vapour pressure reaches 760 torr





Vapour Pressure vs Temperature: Boiling Points of Three Liquids

Boiling Points of Group 16 Hydrides: The Anomaly of Water: A comparison of the boiling points of H_2S , H_2Se , H_2Te , and extrapolated H_2Po against water, showing how hydrogen bonding raises water's boiling point far above the trend expected from London dispersion forces alone



Boiling Points of Group 16 Hydrides: The Anomaly of Water

Short Questions & Answers

Why can gases be compressed much more easily than liquids or solids?

In a gas, molecules are widely separated and about 99.9% of the gas's volume is empty space, so there is a huge amount of space between particles that can be squeezed out under pressure; in liquids and solids, particles are already closely packed together with very little empty space remaining.



Why does the temperature of a gas fall during sudden expansion, the Joule-Thomson effect?

As a gas expands suddenly, its molecules move apart and must do work against the weak attractive forces between them, using up some of their kinetic energy in the process; since temperature is a measure of average kinetic energy, this loss of kinetic energy causes the gas to cool.

Why are London dispersion forces the only intermolecular forces present between nonpolar molecules?

London dispersion forces arise from momentary, randomly fluctuating electron distributions that create instantaneous and induced dipoles in any molecule, polar or nonpolar, while permanent dipole-dipole forces and hydrogen bonding both require a fixed, permanent charge separation that nonpolar molecules do not have.

Why does iodine exist as a solid at room temperature while fluorine and chlorine are gases, even though all three are halogens held together only by London dispersion forces?

London dispersion forces strengthen as molecular size and mass increase, since larger electron clouds are more easily polarized; iodine's much greater molecular mass gives it far stronger London dispersion forces than fluorine or chlorine, strong enough to hold its molecules together as a solid at room temperature.

Why can water form an average of two hydrogen bonds per molecule while ammonia can only form one?

The average number of hydrogen bonds a molecule forms depends on both its number of hydrogen atoms bonded to F, O, or N and its number of available lone pairs; water has two hydrogen atoms and two lone pairs on oxygen, giving an average of two hydrogen bonds, while ammonia has three hydrogen atoms but only one lone pair on nitrogen, limiting it to one hydrogen bond on average.

Why does ice float on liquid water?

As water freezes, its molecules arrange into a regular, extensively hydrogen-bonded tetrahedral lattice that contains more empty space than liquid water does, so the same mass of water occupies about 9% more volume as ice, making ice less dense than liquid water and causing it to float.



Why does water have a much higher boiling point than hydrogen sulfide, even though both are hydrides of group 16 elements?

Oxygen is far more electronegative than sulfur, so water molecules form strong hydrogen bonds with one another, while hydrogen sulfide molecules are held together only by weaker London dispersion and dipole-dipole forces, since sulfur cannot support hydrogen bonding as effectively; overcoming water's stronger intermolecular forces requires much more thermal energy, giving it a far higher boiling point.

Why does surface tension decrease as the temperature of a liquid increases?

Higher temperature gives liquid molecules more kinetic energy, which lets them partially overcome the intermolecular forces of attraction pulling surface molecules inward; with these attractive forces less effective at higher temperature, the inward pull responsible for surface tension weakens.

Why does water boil at a lower temperature at the top of Mount Everest than at sea level?

A liquid boils once its vapour pressure equals the external atmospheric pressure, and atmospheric pressure at high altitude is much lower than at sea level; water's vapour pressure therefore only needs to rise to this lower value to begin boiling, which happens at a correspondingly lower temperature.

Why do crystalline solids have sharp, definite melting points while amorphous solids melt gradually over a range of temperatures?

Crystalline solids have a highly regular, repeating three-dimensional arrangement of particles held together by uniform forces of the same strength throughout, so all the particles are able to break free and melt at essentially the same temperature; amorphous solids lack this long-range order, so different regions of the solid experience slightly different local forces and melt at somewhat different temperatures.



Long Questions & Answers

Explain the different types of intermolecular forces present in liquids, and describe how hydrogen bonding accounts for the unusual, life-sustaining properties of water.

What are London dispersion forces, and what factors affect their strength?

London dispersion forces are momentary forces of attraction that arise when the fluctuating electron cloud of one molecule creates an instantaneous dipole, which induces a temporary dipole in a neighboring molecule; they are the only intermolecular force present between nonpolar molecules, and their strength increases with greater molecular mass and size and with greater molecular surface area, since both make the electron cloud easier to polarize.

What conditions must be met for a hydrogen bond to form, and what determines how many a molecule can form?

A hydrogen bond forms when a hydrogen atom is covalently bonded to a small, highly electronegative atom, fluorine, oxygen, or nitrogen, and is attracted to a lone pair of electrons on a nearby atom of the same type; the average number of hydrogen bonds a molecule can form depends on both the number of hydrogen atoms bonded to F, O, or N and the number of lone pairs available on those atoms.

Why does ice float on liquid water, and why does this matter for aquatic life?

When water freezes, its molecules lock into a regular, extensively hydrogen-bonded tetrahedral lattice containing more empty space than liquid water, so ice occupies about 9% more volume and is less dense than the liquid it forms from, causing it to float; this floating ice layer insulates the water beneath frozen lakes and oceans from the cold air above, letting fish and other aquatic creatures survive through winter.



Why does water have an unusually high heat of vaporization and boiling point compared to other group 16 hydrides?

Based on the trend of increasing London dispersion forces down group 16, water would be expected to have the lowest heat of vaporization and boiling point among the group 16 hydrides, but its extensive hydrogen bonding makes its molecules unusually difficult to separate, giving it the highest heat of vaporization, 40.6 kJ/mol, and boiling point, 100 degrees C, in the group, breaking the expected trend.

How does hydrogen bonding explain water's high surface tension and viscosity?

Water's strong hydrogen bonds create an unusually strong inward pull on molecules at its surface, giving water a high surface tension that lets it form rounded droplets and support small objects like insects; these same strong hydrogen bonds also resist the free movement of water molecules past one another, giving water a higher viscosity than many hydrocarbons and alcohols whose molecules form weaker or no hydrogen bonds.

Describe the properties of gases and derive the ideal gas equation, and explain the differences between crystalline and amorphous solids.

What are the key physical properties of gases, and why do they arise?

Gases have no definite shape or volume and expand to fill their container, because their molecules are widely separated with roughly 99.9% of the gas's volume being empty space; this wide separation also makes gases easy to compress, while gas pressure itself arises entirely from the constant collisions of gas molecules against the walls of their container.

How is the ideal gas equation derived from Boyle's, Charles's, and Avogadro's laws?

Boyle's law states that V is proportional to $1/P$ at constant n and T , Charles's law states that V is proportional to T at constant n and P , and Avogadro's law states that V is proportional to n at constant P and T ; combining all three gives V



proportional to nT/P , which becomes the ideal gas equation, $PV = nRT$, once a constant of proportionality, R , the ideal gas constant, is introduced.

How can the ideal gas equation be used to calculate a gas's relative molecular mass?

Substituting $n = m/M$, where m is the given mass and M is the molar mass, into $PV = nRT$ and rearranging gives $M = mRT/PV$; since the mass, pressure, volume, and temperature of a gas sample can all be measured experimentally, this rearranged equation lets the gas's relative molecular mass be calculated directly.

What distinguishes a crystalline solid from an amorphous solid?

Crystalline solids have a definite, regular, three-dimensional geometric arrangement of particles, giving them a characteristic shape, sharp melting point, definite cleavage planes, and anisotropic properties that depend on measurement direction; amorphous solids lack this long-range order, melting gradually over a range of temperatures, lacking definite cleavage planes, and behaving isotropically, with properties that are the same in every direction.

What is meant by the 'habit' of a crystal, and how can it change?

The habit of a crystal is the characteristic shape in which it usually grows under a given set of conditions; this shape remains consistent as long as the growth conditions stay the same, but it can change if those conditions change, for example, a cubic crystal of sodium chloride grows in a needle-like shape instead if 10% urea is present as an impurity in its solution.

Multiple Choice Questions (MCQs)

Which of the following is held together only by London dispersion forces?

- A. Water molecules in liquid state
- B. Helium atoms in gaseous state
- C. Hydrogen chloride gas molecules
- D. Ammonia molecules in liquid state

Answer: B. Helium atoms in gaseous state

Explanation: Helium is a nonpolar, monoatomic noble gas, so its atoms can only



attract one another through weak, temporary London dispersion forces; water, HCl, and ammonia are all polar and additionally experience dipole-dipole forces or hydrogen bonding.

When the vapour pressure of a liquid becomes equal to the external pressure, the liquid:

- A. Sublimes
- B. Condenses
- C. Boils
- D. Freezes

Answer: C. Boils

Explanation: A liquid boils once its vapour pressure rises to match the external pressure on its surface, allowing bubbles of vapour to form throughout the liquid and escape.

When water freezes at 0 degrees C, its density decreases mainly because of:

- A. A cubic crystal structure
- B. Empty spaces created in the hydrogen-bonded ice structure
- C. A decrease in molecular size
- D. A decrease in viscosity

Answer: B. Empty spaces created in the hydrogen-bonded ice structure

Explanation: As water freezes, its molecules form a regular, extensively hydrogen-bonded tetrahedral lattice that contains more empty space than liquid water, so the same mass occupies a larger volume, lowering the density of ice.

Which sequence correctly ranks these substances in increasing order of molar heat of vaporization?

- A. $\text{H}_2\text{O} > \text{NH}_3 > \text{F}_2$
- B. $\text{F}_2 > \text{NH}_3 > \text{H}_2\text{O}$
- C. $\text{NH}_3 > \text{H}_2\text{O} > \text{F}_2$
- D. $\text{F}_2 < \text{NH}_3 < \text{H}_2\text{O}$

Answer: D. $\text{F}_2 < \text{NH}_3 < \text{H}_2\text{O}$

Explanation: Molar heat of vaporization rises with the strength of intermolecular forces; F_2 has only weak London dispersion forces, NH_3 has weaker hydrogen bonding than water since it has only one lone pair on N, and water's extensive hydrogen bonding gives it the highest heat of vaporization of the three.



Surface tension of a liquid arises mainly from:

- A. An inward pull on surface molecules by molecules below them
- B. An outward push from the liquid's interior
- C. Collisions between vapour molecules
- D. Repulsion between surface molecules

Answer: A. An inward pull on surface molecules by molecules below them

Explanation: Molecules at a liquid's surface are pulled inward by the molecules beneath them through intermolecular attraction, causing the surface to contract and behave like a stretched skin.

Sublimation of solid iodine into iodine vapour involves overcoming mainly:

- A. Ionic bonds
- B. Hydrogen bonds
- C. London dispersion forces
- D. Covalent bonds within the I₂ molecule

Answer: C. London dispersion forces

Explanation: Iodine molecules, I₂, are nonpolar, so they are held to one another in the solid only by London dispersion forces; sublimation only needs to overcome these intermolecular forces, not the strong covalent bond within each I₂ molecule.

Which property is characteristic of crystalline solids but not amorphous solids?

- A. A range of melting temperatures
- B. Isotropic properties
- C. A definite, sharp melting point
- D. Absence of a regular particle arrangement

Answer: C. A definite, sharp melting point

Explanation: Crystalline solids have a definite, regular three-dimensional arrangement of particles held by uniform forces, so they melt sharply at one definite temperature, unlike amorphous solids, which melt gradually over a range of temperatures.

Which of these liquids would be expected to have the highest viscosity at a given temperature?



- A. Water
- B. Ethanol
- C. Diethyl ether
- D. Glycerol, which has three -OH groups per molecule

Answer: D. Glycerol, which has three -OH groups per molecule

Explanation: Viscosity rises with the strength and extent of intermolecular forces; glycerol has three -OH groups per molecule, allowing far more extensive hydrogen bonding than water, ethanol, or diethyl ether, giving it the highest viscosity of the four.

Which type of intermolecular force is present between all molecules, regardless of polarity?

- A. Dipole-dipole forces
- B. Hydrogen bonds
- C. London dispersion forces
- D. Ion-dipole forces

Answer: C. London dispersion forces

Explanation: London dispersion forces arise from momentary, randomly fluctuating electron distributions present in every atom and molecule, so they act between all particles, polar or nonpolar, while dipole-dipole forces, hydrogen bonds, and ion-dipole forces all require a permanent or ionic charge.

Liquid crystals exhibit properties that are:

- A. Only like solids
- B. Only like liquids
- C. Between those of solids and liquids
- D. Unlike either solids or liquids

Answer: C. Between those of solids and liquids

Explanation: Liquid crystals occupy a phase between fully liquid and fully solid: their molecules can migrate and spin like a liquid, but remain roughly parallel to one another in an ordered, crystal-like arrangement rather than moving completely at random.

Quick Revision Summary

- Ideal gas equation: $PV = nRT$, $R = 0.0821 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$; relative molecular mass: $M = mRT/PV$



- Gas pressure arises from molecular collisions with container walls; ideal gases have negligible particle volume and intermolecular forces
- 3 types of intermolecular force: London dispersion (all molecules), permanent dipole-dipole (polar molecules), hydrogen bonding (H bonded to F/O/N with a nearby lone pair)
- London dispersion forces strengthen with greater molecular mass/size and greater surface area
- Hydrogen bonds: strongest intermolecular force, but weaker than ionic/covalent/metallic bonds; number formed depends on H atoms bonded to F/O/N and available lone pairs
- Water forms ~ 2 H-bonds per molecule (2 H atoms, 2 lone pairs); ice is less dense than water due to empty spaces in its hydrogen-bonded lattice ($\sim 9\%$ more volume)
- Water has an anomalously high heat of vaporization (40.6 kJ/mol), boiling point, surface tension, and viscosity, all due to hydrogen bonding
- Surface tension: inward pull on surface molecules; decreases with temperature, increases with stronger IMFs
- Viscosity: resistance to flow; decreases with temperature, increases with stronger IMFs
- Vapour pressure: pressure of vapour in dynamic equilibrium with its liquid; rises with temperature, lower for liquids with stronger IMFs
- Boiling point: temperature where vapour pressure = external pressure; rises with stronger IMFs and higher external pressure
- Molar heat of fusion (solid to liquid) and molar heat of vaporization (liquid to gas) both rise with stronger IMFs
- Crystalline solids: regular geometric shape, sharp melting point, definite cleavage planes, anisotropic; amorphous solids: no long-range order, melt over a range, isotropic
- Liquid crystals: flow and show viscosity like liquids, but have ordered, anisotropic optical properties like solids; used in LCDs, diagnostics, temperature sensors



Exam Tips

- When calculating M from $PV = nRT$, always convert temperature to Kelvin and keep pressure and volume in units matching R , atm and dm^3 , before substituting
- To identify which intermolecular force dominates in a substance, check first for hydrogen bonding, H directly bonded to F, O, or N, then for polarity, permanent dipole-dipole, and only conclude London dispersion forces alone if the molecule is nonpolar
- When comparing boiling points, remember that stronger intermolecular forces always mean a higher boiling point and a lower vapour pressure at a given temperature
- Remember that ice being less dense than water is explained by empty spaces in its hydrogen-bonded lattice, not by any change in the mass or size of the water molecules themselves
- Distinguish crystalline solids from amorphous solids using three quick tests: sharp vs range of melting point, definite cleavage planes vs none, and anisotropic vs isotropic properties
- For boiling point ranking questions, always identify the strongest intermolecular force present in each substance first, since it usually determines the overall order



Chapter 6: Chemical Energetics

Chemical energetics, also called thermochemistry, is the study of the heat absorbed or released during chemical and physical changes, and rests on the idea of enthalpy, a substance's heat content. Every reaction is either exothermic, releasing heat as products end up with lower enthalpy than reactants, or endothermic, absorbing heat as products end up with higher enthalpy; standard enthalpy changes of reaction, combustion, formation, atomization, and neutralization let chemists compare these heat effects on a common footing, and can be calculated from bond energies, measured directly with a calorimeter, or, for reactions that cannot be measured directly, calculated indirectly using Hess's law.

The chapter extends this framework to ionic solids through the Born-Haber cycle, which uses Hess's law to calculate lattice energy from measurable quantities like ionization energy and electron affinity, and to the process of dissolution, where lattice energy and hydration energy together determine whether dissolving a solid in water releases or absorbs heat. It closes by introducing entropy, a measure of disorder that governs whether a process happens spontaneously, and Gibbs free energy, $\Delta G = \Delta H - T\Delta S$, the single quantity that combines enthalpy and entropy to predict, at any temperature, whether a reaction will occur on its own.

Learning Objectives

- Describe chemical reactions as exothermic (ΔH negative) or endothermic (ΔH positive), and interpret an energy profile diagram in terms of ΔH and activation energy
- Define standard conditions and the standard enthalpy changes of reaction, formation, combustion, atomization, and neutralization
- Explain that energy transfer during reactions is due to the breaking and making of bonds, and calculate ΔH from bond energies
- Calculate enthalpy changes from experimental calorimetry results using $q = mc\Delta T$ and $\Delta H = -mc\Delta T/n$



- State and apply Hess's law to calculate enthalpy changes for reactions carried out in multiple steps
- Define lattice energy and enthalpy of hydration, and explain how ionic charge and ionic radius affect their magnitude
- Construct and perform calculations using Born-Haber cycles and energy cycles for enthalpy of solution
- Define entropy and explain how it changes during a change of state, temperature change, or a change in the number of gaseous molecules
- Calculate entropy change for a reaction from standard entropies, and calculate Gibbs free energy change to predict spontaneity
- Explain how enthalpy of combustion relates to the calorie content of food

Key Concepts

6.1 Enthalpy Change: Exothermic and Endothermic Reactions

Enthalpy, denoted H , is the total heat content of a substance, and since every substance has its own characteristic enthalpy, the enthalpy of a reaction's products is never exactly equal to that of its reactants; the difference, $\Delta H = H_{\text{products}} - H_{\text{reactants}}$, is the enthalpy change of the reaction. When products have lower enthalpy than reactants, ΔH is negative and heat is released to the surroundings, an exothermic process, as in the combustion of carbon in oxygen, $\Delta H = -393.7 \text{ kJ/mol}$; when products have higher enthalpy than reactants, ΔH is positive and heat is absorbed from the surroundings, an endothermic process, as in the dissolution of ammonium chloride in water, $\Delta H = +16.2 \text{ kJ/mol}$, the basis of instant cold packs.

6.2 Energy Profile Diagrams and Activation Energy

Before reactant bonds can break and product bonds can form, colliding reactant molecules must possess a minimum amount of energy, called the activation energy (E_a), needed to cross an energy barrier; an energy profile diagram plots this journey, showing reactants rising to a high-energy transition state before falling to products, with the overall height difference between reactants and products representing ΔH . In an exothermic reaction, the products sit at lower energy than the reactants on this diagram, while in an endothermic



reaction the products sit higher, but both reactions still require an initial input of activation energy to get started.

6.3 Standard Enthalpy Changes

Because enthalpy depends on physical state, temperature, and pressure, meaningful comparisons require standard conditions, a temperature of 25 degrees C (298 K) and a pressure of 1 atm (101 kPa); the standard state of an element is its most stable form under these conditions, for example graphite rather than diamond for carbon, and by definition the standard enthalpy of formation of any element in its standard state is zero. Several named standard enthalpy changes are used throughout thermochemistry: standard enthalpy of reaction (ΔH°_r), the enthalpy change when stoichiometric amounts of reactants in their standard states react completely to form products; standard enthalpy of combustion (ΔH°_c), always exothermic, the enthalpy change when one mole of a substance burns completely in excess oxygen; and standard enthalpy of formation (ΔH°_f), the enthalpy change when one mole of a compound forms from its elements.

Two further standard enthalpy changes complete the set: standard enthalpy of atomization (ΔH°_{at}), the enthalpy change when one mole of gaseous atoms forms from an element, such as $\frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{H}(\text{g})$, $\Delta H^\circ_{at} = +218 \text{ kJ/mol}$; and standard enthalpy of neutralization (ΔH°_n), always exothermic, the enthalpy change when one mole of water forms from the reaction of an acid with an alkali, which is essentially the same for every strong acid-strong base reaction, close to -57.1 kJ/mol , because the only chemical change occurring is $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$, with the other ions remaining as spectators in solution. First electron affinity, the enthalpy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous uni-negative ions, is also measured under standard conditions and is usually negative, since energy is released.

6.4 Bond Energy and Enthalpy Changes

Bond dissociation energy is the average energy required to break one mole of a particular bond; because breaking bonds always absorbs energy (ΔH positive) while forming bonds always releases it (ΔH negative), the overall sign of a reaction's enthalpy change depends on which effect wins, with a



reaction being exothermic if more energy is released forming new bonds than was absorbed breaking old ones. Bond energies for a specific bond in a specific molecule, called exact bond energies, vary slightly from compound to compound, so tabulated values are usually average bond energies; the enthalpy change of a gas-phase reaction can then be estimated as $\Delta H^\circ_r = (\text{sum of bond energies broken in reactants}) - (\text{sum of bond energies formed in products})$.

6.5 Measuring Enthalpy Change: Calorimetry

The heat evolved or absorbed during a reaction can be measured using a calorimeter, an insulated vessel fitted with a stirrer and thermometer; a simple glass calorimeter is suitable for reactions in solution, though not for reactions involving gases or very high temperatures, and works by measuring the temperature change of the solution, whose heat capacity is approximated by that of water, using $q = m \times c \times \Delta T$, where c is specific heat capacity, 4.18 J/g K for water, often rounded to 4.2. The enthalpy change per mole is then found using $\Delta H = -q/n$, or equivalently $-mc\Delta T/n$, where n is the number of moles of the limiting reactant or product formed, with the negative sign reflecting that a temperature rise, heat evolved by the reaction, corresponds to an exothermic, negative ΔH .

6.6 Enthalpy and the Calorie Content of Food

Food acts as a fuel: the chemical energy released when food is digested in the body is the same as the energy released when it is burned outside the body, so a food's calorie content can be found from its standard enthalpy of combustion, typically measured in a bomb calorimeter, using $\text{calorie content (kcal/g)} = \Delta H^\circ \text{ (kJ/g)} / 4.184$. For glucose, whose combustion releases 2803 kJ per mole, 180 g, this works out to about 15.57 kJ/g, or roughly 3.72 kcal/g; because the body must balance the calories it takes in from food with the energy it expends through activity, this enthalpy-based calorie content underlies the basic principle of energy balance in nutrition.

6.7 Hess's Law of Heat Summation

Hess's law, a direct consequence of the first law of thermodynamics, conservation of energy, states that the total enthalpy change of a reaction is



independent of the route by which it occurs, as long as the initial and final conditions are the same; this makes it possible to calculate ΔH for reactions that cannot be measured directly, such as the formation of CCl_4 from carbon and chlorine, by combining the enthalpy changes of a series of steps that connect the same reactants and products, often visualized as an enthalpy cycle. If a reaction can proceed by a direct route or by an indirect route through intermediates, the sum of the enthalpy changes around the indirect route must equal the enthalpy change of the direct route.

Hess's law has several standard applications: calculating an enthalpy of formation from enthalpies of combustion, as for carbon monoxide, where $\Delta H_f = \Delta H_{\text{combustion}}(\text{C}) - \Delta H_{\text{combustion}}(\text{CO}) = -393.5 - (-283) = -110.5 \text{ kJ/mol}$; calculating an enthalpy of reaction from enthalpies of formation of reactants and products; and calculating an enthalpy of reaction from bond energies, treating bond-breaking and bond-forming as a hypothetical two-step process. In every case, the same underlying principle applies: ΔH for the direct reaction equals the sum of the ΔH values for any indirect path connecting the same starting and ending points.

6.8 Energetics of Solution: Hydration and Lattice Energy

Dissolving an ionic solid involves two opposing energy effects: breaking apart the ionic lattice, which requires energy equal in magnitude to the lattice energy, and hydrating the freed ions, which releases energy equal to the enthalpy of hydration; the standard enthalpy of solution ($\Delta H^\circ_{\text{sol}}$) is the net heat absorbed or released when one mole of a substance dissolves to form an infinitely dilute solution, and the three quantities are related by $\Delta H^\circ_{\text{latt}} + \Delta H^\circ_{\text{sol}} = \Delta H^\circ_{\text{hyd}}$. Hydration is the process in which water molecules surround and interact with solute ions through ion-dipole forces, and its magnitude depends on the ion's charge density, charge per unit surface area, with smaller, more highly charged ions having larger, more exothermic, hydration energies.

Lattice energy, the enthalpy change when one mole of an ionic compound forms from its gaseous ions, similarly depends on ionic charge and ionic radius: lattice energy becomes less exothermic, weaker, as ionic size increases, since larger ions cannot pack as closely together, and becomes more exothermic, stronger,



as ionic charge increases, which is why magnesium oxide, $\Delta H^\circ_{\text{latt}} = -3923$ kJ/mol, from doubly-charged ions, has a far larger lattice energy than lithium fluoride, $\Delta H^\circ_{\text{latt}} = -1049$ kJ/mol, from singly-charged ions of similar size. The balance between these two competing factors also explains solubility trends down a group: for group 2 hydroxides, lattice energy falls faster than hydration energy down the group, making $\Delta H^\circ_{\text{sol}}$ more exothermic and solubility increase, while for group 2 sulfates, hydration energy falls faster, making $\Delta H^\circ_{\text{sol}}$ more endothermic and solubility decrease.

6.9 The Born-Haber Cycle

Lattice energy cannot be measured directly in a single experiment, but it can be calculated indirectly using the Born-Haber cycle, an application of Hess's law that connects the standard enthalpy of formation of an ionic compound to a sequence of measurable steps: atomization of the metal, ionization of the metal atom, atomization of the nonmetal, and electron affinity of the nonmetal, followed by the formation of the solid lattice from gaseous ions. Applying Hess's law around the complete cycle, $\Delta H^\circ_{\text{f}} = \Delta H_{\text{x}} + \Delta H^\circ_{\text{latt}}$, where ΔH_{x} is the sum of the atomization, ionization, and electron affinity steps, lets the otherwise unmeasurable lattice energy be calculated once every other quantity in the cycle is known, as for sodium chloride, where $\Delta H^\circ_{\text{latt}} = \Delta H^\circ_{\text{f}} - \Delta H_{\text{x}} = -411 - 376 = -787$ kJ/mol.

6.10 Entropy

Entropy (S) is a measure of the number of ways in which the energy and particles of a system can be arranged, and is often described as a measure of disorder or randomness; a system becomes energetically more stable as it becomes more disordered, since a greater number of possible arrangements is statistically more probable. This can be shown by counting arrangements directly: if 3 gas molecules initially confined to one jar are allowed to diffuse between two connected jars, there are 2^3 , or 8, possible arrangements, and in general, x^y possible arrangements exist for y particles distributed among x locations, so entropy rises sharply as the number of particles increases.

Entropy values can be compared using a few general rules: substances with more particles have higher entropy than those with fewer, CaCO_3 , with more



atoms per formula unit, has higher standard entropy than CaO; harder, more rigid substances have lower entropy than softer ones with the same chemical composition, diamond has lower entropy than graphite; and a substance has progressively higher entropy as it moves from solid to liquid to gas, ice, liquid water, and steam have standard entropies of 48.0, 69.9, and 188.7 J/K/mol respectively. In a chemical reaction, entropy tends to increase whenever a solid converts to a liquid or gas, or whenever the number of moles of gas increases from reactants to products, since gas molecules have far more possible arrangements than the same number of particles in a liquid or solid.

6.11 Calculating Entropy Change and Predicting Spontaneity

The entropy change of a reaction system is calculated the same way as enthalpy change, $\Delta S^\circ_{\text{system}} = (\text{sum of } S^\circ \text{ of products}) - (\text{sum of } S^\circ \text{ of reactants})$, using standard molar entropies weighted by the stoichiometric coefficients in the balanced equation. However, the entropy change of the system alone does not determine spontaneity; the entropy change of the surroundings, calculated as $\Delta S^\circ_{\text{surroundings}} = -\Delta H^\circ_{\text{reaction}}/T$, with $\Delta H^\circ_{\text{reaction}}$ converted to joules, must be added to it to give the total entropy change, $\Delta S^\circ_{\text{total}} = \Delta S^\circ_{\text{system}} + \Delta S^\circ_{\text{surroundings}}$, and a reaction is spontaneous only if $\Delta S^\circ_{\text{total}}$ is positive.

Multiplying the total entropy change by $-T$ gives the Gibbs free energy change, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, a single quantity that predicts spontaneity without needing to separately calculate the entropy change of the surroundings: a reaction is spontaneous if ΔG° is negative, non-spontaneous if ΔG° is positive, and at equilibrium if ΔG° is exactly zero. Because ΔG° depends on temperature through the $-T\Delta S^\circ$ term, the sign combinations of ΔH° and ΔS° determine four possible temperature behaviors: a reaction with negative ΔH° and positive ΔS° is spontaneous at all temperatures, one with positive ΔH° and negative ΔS° is never spontaneous, and reactions with matching signs of ΔH° and ΔS° , both negative or both positive, switch from spontaneous to non-spontaneous, or vice versa, at some particular temperature.



Important Definitions

What is enthalpy (H)?

The total heat content of a substance, comprising all its potential and kinetic energies.

What is an exothermic process?

A reaction or physical change in which heat is evolved from the system to the surroundings (ΔH negative).

What is an endothermic process?

A reaction or physical change in which heat is absorbed by the system from the surroundings (ΔH positive).

What is activation energy (E_a)?

The minimum energy that colliding reactant molecules must possess to cross the energy barrier and react.

What is standard enthalpy of formation (ΔH°_f)?

The enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.

What is bond dissociation energy?

The average energy required to break one mole of a particular bond in a substance.

What is Hess's law?

The principle that the total enthalpy change of a reaction is independent of the route taken, provided the initial and final conditions are the same.

What is lattice energy (ΔH°_{latt})?

The enthalpy change when one mole of an ionic compound is formed from its gaseous ions under standard conditions.

What is entropy (S)?

A measure of the number of possible arrangements of the particles and energy of a system; often described as a measure of disorder.

What is Gibbs free energy change (ΔG)?

A quantity, $\Delta G = \Delta H - T\Delta S$, whose sign predicts whether a process can occur spontaneously.



Key Facts and Relations

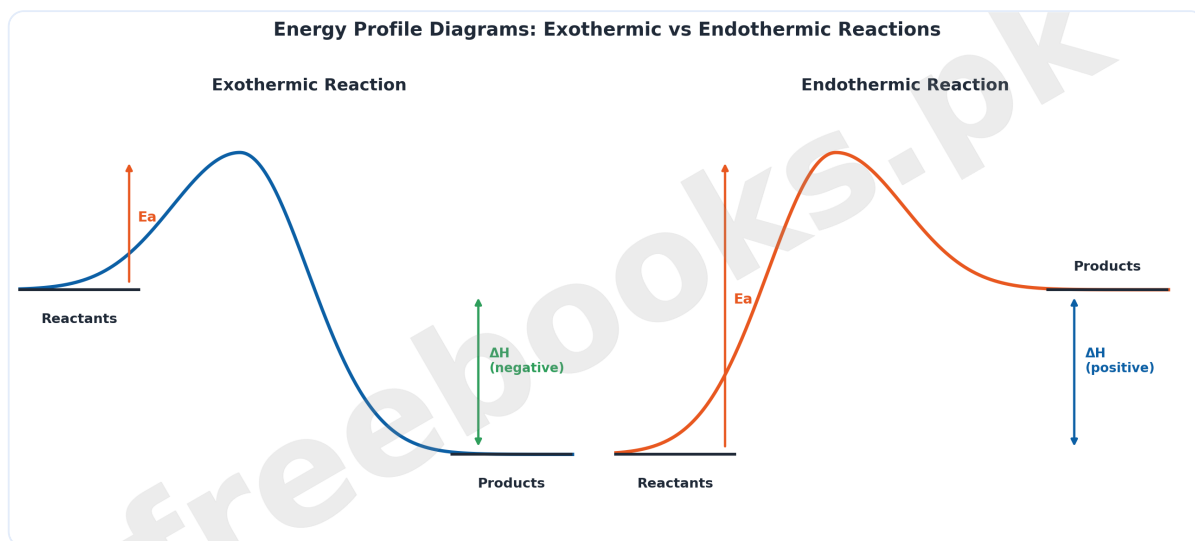
Topic	Key Fact / Relation
Enthalpy change	$\Delta H = H_{\text{products}} - H_{\text{reactants}}$
Enthalpy from bond energies	$\Delta H^{\circ}_r = \sum(E, \text{ bonds broken}) - \sum(E, \text{ bonds formed})$
Calorimetry heat	$q = m \times c \times \Delta T$
Calorimetry enthalpy change	$\Delta H = -q/n = -mc\Delta T/n$
Calorie content of food	$\text{Calorie content (kcal/g)} = \Delta H^{\circ} \text{ (kJ/g)} / 4.184$
Hess's law (enthalpy cycle)	$\Delta H \text{ (direct route)} = \text{sum of } \Delta H \text{ (indirect route steps)}$
Enthalpy of solution cycle	$\Delta H^{\circ}_{\text{latt}} + \Delta H^{\circ}_{\text{sol}} = \Delta H^{\circ}_{\text{hyd}}$
Born-Haber cycle	$\Delta H^{\circ}_f = \Delta H_x + \Delta H^{\circ}_{\text{latt}}$
Entropy change of system	$\Delta S^{\circ}_{\text{system}} = \sum S^{\circ}_{\text{products}} - \sum S^{\circ}_{\text{reactants}}$
Gibbs free energy	$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

Diagrams

Energy Profile Diagrams: Exothermic vs Endothermic Reactions: A

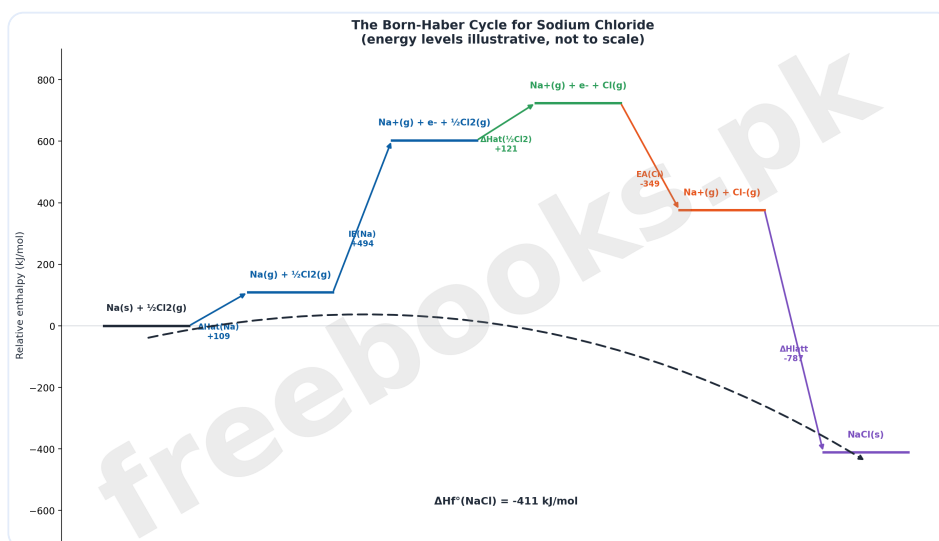
comparison of reaction-coordinate diagrams for exothermic and endothermic reactions, showing activation energy (E_a) as the barrier height and ΔH as the difference between reactant and product energy levels





Energy Profile Diagrams: Exothermic vs Endothermic Reactions

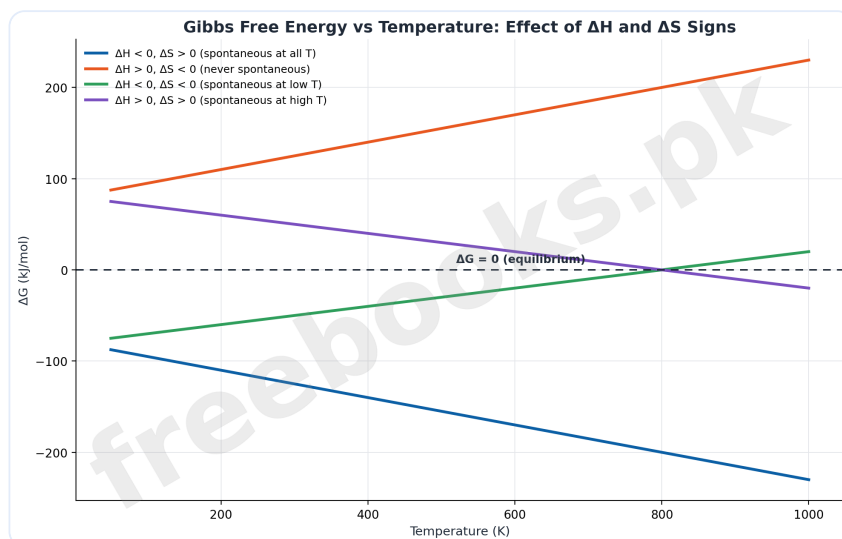
The Born-Haber Cycle for Sodium Chloride: A step-by-step energy cycle showing how the standard enthalpy of formation of NaCl relates to atomization, ionization, electron affinity, and lattice energy, illustrating how lattice energy is calculated indirectly using Hess's law



The Born-Haber Cycle for Sodium Chloride

Gibbs Free Energy vs Temperature: Effect of Delta H and Delta S Signs: A plot of Delta G against temperature for the four possible sign combinations of Delta H and Delta S, showing which reactions are spontaneous at all temperatures, never spontaneous, or spontaneous only above or below a particular temperature





Gibbs Free Energy vs Temperature: Effect of Delta H and Delta S Signs

Short Questions & Answers

Why is the combustion of carbon in oxygen described as exothermic?

The reaction releases heat to the surroundings because the total enthalpy of the products, carbon dioxide, is lower than the total enthalpy of the reactants, carbon and oxygen; this lowering of enthalpy, $\Delta H = -393.7 \text{ kJ/mol}$, is evolved as heat, making the reaction exothermic.

Why do both exothermic and endothermic reactions require activation energy?

Regardless of whether the overall reaction releases or absorbs energy, the colliding reactant molecules must still possess enough energy to overcome an energy barrier before their bonds can break and new bonds can form; this minimum required energy, the activation energy, must be supplied at the start of any reaction.

Why is the standard enthalpy of formation of an element in its standard state defined as zero?

Standard enthalpy of formation measures the enthalpy change of forming a substance from its elements; since an element in its own standard state is already the reference starting material for itself, there is no chemical change and therefore no enthalpy change involved, giving a value of zero by definition.

Why is the enthalpy of neutralization nearly the same, about -57.1 kJ/mol , for every strong acid-strong base reaction?



For a strong acid and a strong base, the only chemical change occurring on mixing is the combination of H^+ and OH^- ions to form water, $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$; the other ions present remain as spectator ions in solution, so the same fundamental reaction, and therefore essentially the same enthalpy change, occurs regardless of which strong acid or base is used.

Why does an average, rather than exact, bond energy have to be used in most calculations?

The energy of a particular type of bond, such as C-C, varies slightly depending on which other atoms and bonds are present in the rest of the molecule, so an exact bond energy is only valid for one specific compound; an average bond energy, calculated across many different molecules containing that bond, gives a more generally applicable value for estimating enthalpy changes.

Why is Hess's law useful for reactions like the formation of CCl_4 from carbon and chlorine, which cannot be measured directly by a calorimeter?

Hess's law states that the total enthalpy change of a reaction depends only on the initial and final states, not on the route taken; this means the enthalpy change of a reaction that cannot be carried out or measured directly can instead be calculated by combining the enthalpy changes of a series of other, measurable reactions that connect the same starting reactants and final products.

Why does the lattice energy of magnesium oxide ($\Delta H^\circ_{\text{latt}} = -3923 \text{ kJ/mol}$) greatly exceed that of lithium fluoride ($\Delta H^\circ_{\text{latt}} = -1049 \text{ kJ/mol}$), despite similar ion sizes?

Lattice energy rises sharply with increasing ionic charge; magnesium oxide is built from doubly-charged Mg^{2+} and O^{2-} ions, which attract each other far more strongly through electrostatic force than the singly-charged Li^+ and F^- ions of lithium fluoride, giving MgO a much larger, more exothermic lattice energy.

Why can lattice energy not be measured directly in a single experiment?

Lattice energy is defined as the enthalpy change when an ionic solid forms from free gaseous ions, a process that cannot be carried out or observed directly in the laboratory; instead, it must be calculated indirectly using a Born-Haber cycle,



which relates it to a series of other quantities that can each be measured experimentally.

Why does the entropy of water vapour exceed that of liquid water, which in turn exceeds that of ice?

Entropy reflects the number of ways a substance's particles and energy can be arranged; a gas has far more freedom of motion and far more possible arrangements than a liquid, which in turn has more freedom and possible arrangements than the fixed, ordered positions of a solid, so entropy rises in the order solid, liquid, gas.

Why is a reaction with negative ΔH and negative ΔS spontaneous only at low temperature?

In $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, a negative ΔS° makes the $-T\Delta S^\circ$ term positive and this positive contribution grows larger as temperature increases; at low temperature this term is small enough that the negative ΔH° still dominates, making ΔG° negative and the reaction spontaneous, but at high temperature the growing positive $-T\Delta S^\circ$ term eventually overtakes ΔH° , making ΔG° positive and the reaction non-spontaneous.

Long Questions & Answers

Explain the different standard enthalpy changes used in thermochemistry, and describe how Hess's law allows enthalpy changes to be calculated indirectly.

Why must standard conditions be specified when comparing enthalpy changes?

Enthalpy depends on a substance's physical state, temperature, and pressure, so different measurements of the same reaction could give different results unless these conditions are fixed; standard conditions, a temperature of 25 degrees C, 298 K, and a pressure of 1 atm, provide a common reference point that allows enthalpy changes of different reactions to be meaningfully compared.



What is the difference between standard enthalpy of formation and standard enthalpy of combustion?

Standard enthalpy of formation is the enthalpy change when one mole of a compound forms from its elements in their standard states, and can be positive or negative; standard enthalpy of combustion is the enthalpy change when one mole of a substance burns completely in excess oxygen, and is always exothermic, always negative.

What is standard enthalpy of atomization, and why is it always positive?

Standard enthalpy of atomization is the enthalpy change when one mole of gaseous atoms is formed from an element under standard conditions; it is always positive because breaking the bonds holding an element's atoms together, whether covalent bonds in a molecule or metallic bonding in a solid, always requires an input of energy.

What is Hess's law, and why does it follow from the conservation of energy?

Hess's law states that the total enthalpy change of a reaction is independent of the route taken, as long as the initial and final conditions are the same; this follows directly from the conservation of energy, since if two different routes between the same starting and ending points gave different total enthalpy changes, energy could be created or destroyed simply by choosing one route over the other, which is impossible.

How is Hess's law applied to calculate an enthalpy of formation from enthalpies of combustion?

An enthalpy cycle is drawn connecting the elements, the target compound, and the final combustion products by two different routes, one direct and one indirect via combustion; since the total enthalpy change must be the same by either route, the unknown enthalpy of formation can be found by rearranging the equation relating the known combustion enthalpies to the direct enthalpy of combustion of the target compound.



Describe the Born-Haber cycle and explain how entropy and Gibbs free energy together determine whether a reaction occurs spontaneously.

What is the Born-Haber cycle, and why is it needed to find lattice energy?

The Born-Haber cycle is an energy cycle, based on Hess's law, that connects the standard enthalpy of formation of an ionic compound to a sequence of measurable steps, atomization, ionization, and electron affinity, followed by lattice formation; it is needed because lattice energy itself, the enthalpy change of forming a solid from gaseous ions, cannot be measured directly in any single experiment.

What is entropy, and how is it related to the number of possible arrangements of a system?

Entropy is a measure of the number of ways the particles and energy of a system can be arranged; systems with more possible arrangements, more disorder, are statistically more probable and therefore more stable, which is why gases, with far more freedom of movement, have higher entropy than liquids or solids of the same substance.

Why is the entropy change of the system alone not enough to predict spontaneity?

A reaction's overall spontaneity depends on the total entropy change of both the system and its surroundings, not the system alone; some reactions, like the formation of calcium oxide, have a negative entropy change in the system but proceed spontaneously anyway because they release enough heat to the surroundings to increase the surroundings' entropy by an even larger amount, making the total entropy change positive.

How does the Gibbs free energy equation combine enthalpy and entropy to predict spontaneity?

The Gibbs free energy change, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, is derived by multiplying the total entropy change by $-T$, so it captures the combined effect of the reaction's own enthalpy change and its entropy change without needing to



separately calculate the entropy change of the surroundings; a reaction is spontaneous if ΔG° is negative, non-spontaneous if positive, and at equilibrium if exactly zero.

Why can a reaction with positive ΔH and positive ΔS become spontaneous only at high temperature?

In $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, a positive ΔS° makes the $-T\Delta S^\circ$ term negative, and this negative contribution grows larger in magnitude as temperature rises; at low temperature this term is too small to outweigh the positive ΔH° , keeping ΔG° positive and the reaction non-spontaneous, but at sufficiently high temperature the growing negative $-T\Delta S^\circ$ term overtakes ΔH° , making ΔG° negative and the reaction spontaneous.

Multiple Choice Questions (MCQs)

Which of the following equations represents the standard enthalpy of formation of C_2H_4 ?

- A. $2C(\text{diamond}) + 2H_2(g) \rightarrow C_2H_4(g)$
- B. $2C(\text{graphite}) + 2H_2(g) \rightarrow C_2H_4(g)$
- C. $C(\text{graphite}) + H_2(g) \rightarrow \frac{1}{2} C_2H_4(g)$
- D. $2C(\text{diamond}) + 4H(g) \rightarrow C_2H_4(g)$

Answer: B. $2C(\text{graphite}) + 2H_2(g) \rightarrow C_2H_4(g)$

Explanation: Standard enthalpy of formation requires elements in their standard states; carbon's standard state is graphite, not diamond, and the equation must form exactly one mole of the compound from whole numbers of moles of elements, matching only option B.

Which equation correctly defines the lattice energy of $MgCl_2$?

- A. $Mg(s) + Cl_2(g) \rightarrow MgCl_2$
- B. $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(g)$
- C. $Mg^{2+}(s) + 2Cl^-(g) \rightarrow MgCl_2(s)$
- D. $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$

Answer: D. $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$

Explanation: Lattice energy is defined as the enthalpy change when one mole of an ionic solid forms from its gaseous ions; only option D shows gaseous Mg^{2+} and Cl^- ions combining to form solid $MgCl_2$.



If 100 molecules of a gas are initially confined to jar A, connected to an evacuated jar B, the number of possible arrangements once the stopcock is opened is:

- A. 100
- B. $1/100$
- C. 2^{100}
- D. $1/2^{100}$

Answer: C. 2^{100}

Explanation: The number of possible arrangements of y particles among x available locations is x^y ; with 2 jars available to 100 molecules, this gives 2^{100} possible arrangements.

For a reaction to occur spontaneously, which condition must be satisfied?

- A. $(\Delta H - T\Delta S)$ must be negative
- B. $(\Delta H + T\Delta S)$ must be negative
- C. ΔH must be negative
- D. ΔS must be negative

Answer: A. $(\Delta H - T\Delta S)$ must be negative

Explanation: A reaction is spontaneous when ΔG is negative, and $\Delta G = \Delta H - T\Delta S$, so it is this combined quantity, not ΔH or ΔS alone, that must be negative.

The calorie content of food is fundamentally related to which thermodynamic quantity?

- A. Entropy change (ΔS)
- B. Gibbs free energy change (ΔG)
- C. Enthalpy change (ΔH)
- D. Specific heat capacity (c)

Answer: C. Enthalpy change (ΔH)

Explanation: Calorie content is calculated directly from a food's standard enthalpy of combustion, ΔH° , converted from kJ/g into kcal/g.

Which of the following is NOT typically determined using Hess's law?

- A. Enthalpy change of formation
- B. Enthalpy change of combustion
- C. Activation energy



D. Enthalpy change of reaction

Answer: C. Activation energy

Explanation: Hess's law relates different enthalpy changes, ΔH values, to one another through enthalpy cycles; activation energy is a kinetic quantity related to reaction rate, not an enthalpy change, and is not calculated using Hess's law.

Which combination of factors would give the most exothermic (greatest magnitude) enthalpy of hydration?

- A. A larger ionic radius and a smaller charge
- B. A smaller ionic radius and a smaller charge
- C. A larger ionic radius and a larger charge
- D. A smaller ionic radius and a larger charge

Answer: D. A smaller ionic radius and a larger charge

Explanation: Hydration energy rises with charge density, charge per unit surface area; a smaller ion with a larger charge has the highest charge density of the four combinations, giving the most exothermic enthalpy of hydration.

The enthalpy of solution can be expressed in terms of which combination of enthalpy changes?

- A. $\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$
- B. $\Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$
- C. $-\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$
- D. $-\Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$

Answer: A. $\Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$

Explanation: The energy cycle relating these quantities gives $\Delta H^{\circ}_{\text{latt}} + \Delta H^{\circ}_{\text{sol}} = \Delta H^{\circ}_{\text{hyd}}$, which rearranges to $\Delta H^{\circ}_{\text{sol}} = \Delta H^{\circ}_{\text{hyd}} - \Delta H^{\circ}_{\text{latt}}$; written the other way, $\Delta H^{\circ}_{\text{hyd}} = \Delta H^{\circ}_{\text{latt}} + \Delta H^{\circ}_{\text{sol}}$, matching option A's combination of the two enthalpy changes.

Which of the following reactions has an enthalpy change equal to the standard enthalpy of formation of liquid water?

- A. $2\text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- B. $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$
- C. $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- D. $2\text{H}^+(\text{aq}) + \text{O}_2^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

Answer: C. $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$



Explanation: Standard enthalpy of formation requires the elements in their standard states, gaseous H_2 and O_2 , combining to form one mole of the compound in its standard state, liquid water; only option C matches both requirements.

Which of the following processes would typically result in an increase in the entropy of the system?

- A. Freezing of water
- B. Condensation of steam
- C. Dissolving a solid in a liquid
- D. Formation of a crystal from a saturated solution

Answer: C. Dissolving a solid in a liquid

Explanation: Dissolving a solid disperses its ordered particles throughout the solvent, greatly increasing the number of possible arrangements and therefore the entropy of the system, unlike freezing, condensation, or crystallization, which all decrease disorder.

Quick Revision Summary

- Enthalpy change: $\Delta H = H_{\text{products}} - H_{\text{reactants}}$; exothermic (ΔH negative, heat released) vs endothermic (ΔH positive, heat absorbed)
- Energy profile diagrams show activation energy (E_a) as the barrier height and ΔH as reactant-product energy difference
- Standard conditions: 25 degrees C (298 K), 1 atm; standard enthalpy of formation of an element in its standard state = 0
- Named standard enthalpy changes: reaction, combustion (always exothermic), formation, atomization (always endothermic), neutralization (always exothermic, ~ -57.1 kJ/mol), electron affinity
- ΔH°_r from bond energies = $\sum(E, \text{ bonds broken}) - \sum(E, \text{ bonds formed})$
- Calorimetry: $q = mc\Delta T$; $\Delta H = -q/n = -mc\Delta T/n$
- Calorie content (kcal/g) = ΔH° (kJ/g) / 4.184
- Hess's law: total ΔH is route-independent; used to find ΔH_f from combustion data, ΔH_r from formation data, and ΔH_r from bond energies
- Enthalpy of solution cycle: $\Delta H^\circ_{\text{latt}} + \Delta H^\circ_{\text{sol}} = \Delta H^\circ_{\text{hyd}}$; hydration and lattice energy both rise with charge density (charge/size)



- Born-Haber cycle: $\Delta H^\circ_f = \Delta H_x + \Delta H^\circ_{\text{latt}}$, used to calculate the otherwise unmeasurable lattice energy
- Entropy (S): measure of possible arrangements/disorder; solid < liquid < gas; rises with more particles, more gas moles, softer substances
- $\Delta S^\circ_{\text{system}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$; $\Delta S^\circ_{\text{surroundings}} = -\Delta H^\circ_{\text{reaction}}/T$; $\Delta S^\circ_{\text{total}} = \Delta S^\circ_{\text{system}} + \Delta S^\circ_{\text{surroundings}}$
- Reaction spontaneous if $\Delta S^\circ_{\text{total}}$ is positive, equivalently if $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is negative
- 4 sign combinations of $\Delta H/\Delta S$ determine temperature-dependence of spontaneity (see Gibbs free energy vs temperature diagram)

Exam Tips

- Always double-check that an equation matches the exact definition of the named enthalpy change being asked about (formation, combustion, atomization, neutralization) -- exam questions often test whether the equation uses the correct standard states and exactly 1 mole of the right substance
- When calculating ΔH from bond energies, always subtract energy of bonds formed from energy of bonds broken, not the other way around -- getting this backwards flips the sign of the answer
- For calorimetry questions, convert q from J to kJ before dividing by moles, and remember the negative sign in $\Delta H = -q/n$ reflects that a temperature rise (heat released by the reaction) means the reaction itself is exothermic
- When solving Hess's law problems, draw the enthalpy cycle first and label every arrow with its direction and value before writing any equation -- this prevents sign errors when combining steps
- Remember hydration energy and lattice energy both become more exothermic with smaller ionic radius and greater ionic charge -- use charge density (charge per unit size) as the single factor that predicts both
- For spontaneity questions, always convert ΔH to the same energy units as $T\Delta S$ (usually kJ) before combining them in $\Delta G = \Delta H - T\Delta S$, since ΔS is normally given in J/K, not kJ/K



Chapter 7: Reaction Kinetics

Reaction kinetics is the branch of chemistry that studies how fast chemical reactions occur and what factors control that speed, from reactions that appear instantaneous, such as sodium chloride reacting with silver nitrate, to reactions that take years, such as iron rusting. Collision theory explains this range: a reaction can only occur when reactant particles collide with the correct orientation and with at least a minimum amount of energy, the activation energy, needed to break existing bonds and begin forming new ones; only a small fraction of all collisions satisfy both conditions and are therefore effective.

Building on this foundation, the chapter introduces the rate law, an experimentally determined equation relating the rate of a reaction to reactant concentrations through a rate constant and an order of reaction, and shows how this rate constant can be calculated using either the initial concentration method or, for first order reactions, the simpler half-life method. It closes by looking beneath the overall balanced equation at the reaction mechanism, the sequence of elementary steps by which a reaction actually proceeds, and shows how the slowest of these steps, the rate-determining step, controls the observed rate law of the whole reaction.

Learning Objectives

- Describe collision theory and explain the role of activation energy and molecular orientation in determining whether a collision is effective
- Define the rate of a reaction and distinguish between its average rate and its instantaneous rate at a point in time
- Describe the chemical and physical methods used to measure the concentration of a reactant or product during a reaction
- Explain, using collision theory and the Maxwell-Boltzmann distribution, how concentration, temperature, surface area, and catalysts each affect reaction rate
- Write and interpret a rate law (rate equation) of the form $\text{Rate} = k[\text{A}]^x[\text{B}]^y$, and define the rate constant, k



- Define order of reaction with respect to a single reactant and overall, and identify zero, first, second, third, and fractional order reactions
- Derive the units of the rate constant for a reaction of any given order
- Calculate the rate constant of a reaction using the initial concentration (initial rate) method and the half-life method
- Describe a reaction mechanism in terms of elementary steps, molecularity, and reaction intermediates
- Identify the rate-determining step of a proposed mechanism and use it to deduce the reaction's rate law

Key Concepts

7.1 Collision Theory and Activation Energy

Different reactions proceed at vastly different speeds: the precipitation of silver chloride from sodium chloride and silver nitrate solutions is essentially instantaneous, the acid-catalyzed hydrolysis of an ester takes minutes to hours, and the rusting of iron takes months or years. Collision theory explains this range by proposing that a reaction can only occur when reactant particles collide, and that not every collision leads to a reaction: the colliding particles must be oriented correctly relative to one another so that the necessary bonds can break and form, and together they must possess at least a minimum amount of energy, the activation energy (E_a), needed to reach the high-energy transition state between reactants and products. Collisions that satisfy both conditions are called effective or successful collisions, and only a small fraction of all collisions occurring in a reaction mixture typically meet this standard at any given moment.

7.2 Rate of Reaction: Average and Instantaneous Rate

The rate of a chemical reaction is defined as the change in concentration of a reactant or product per unit time, $\text{Rate} = \Delta x / \Delta t$, where Δx is the change in concentration (mol dm^{-3}) and Δt is the time interval (s), giving the rate units of $\text{mol dm}^{-3} \text{ s}^{-1}$; because reactant concentration falls and product concentration rises as a reaction proceeds, rate is conventionally reported as a positive quantity regardless of which species is being tracked. The average rate over a stated time interval is simply the total change in concentration divided by



that interval, but because the concentration-time graph of a reaction is curved rather than straight, the rate itself changes continuously as the reaction proceeds, generally slowing as reactant concentration falls.

The instantaneous rate at any particular moment is found graphically, by plotting concentration against time and drawing a tangent to the curve at the point of interest; the slope of this tangent gives the instantaneous rate at that instant. This graphical, tangent-slope method was demonstrated historically using the decomposition of hydrogen iodide, where concentration-time data was plotted and a tangent drawn at a chosen point gave an instantaneous rate of about $4 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$, distinct from the average rate calculated over the whole experiment.

7.3 Measuring Concentration During a Reaction

Following a reaction's progress requires measuring how the concentration of a reactant or product changes with time, and this can be done using either chemical or physical methods. The chemical method withdraws a small sample of the reaction mixture at set time intervals and analyzes it by titration, for example titrating the acid produced during ester hydrolysis against sodium hydroxide using phenolphthalein indicator; because each titration takes time and consumes part of the sample, this method gives discontinuous data points and can disturb the reaction being studied.

Physical methods instead monitor a property of the reaction mixture that changes continuously and can be measured without removing or disturbing any sample, making them generally preferable when applicable. These include spectrophotometry or colorimetry, which tracks the change in colour intensity or light absorbance of a coloured reactant or product; electrical conductivity, which tracks the change in concentration of ions in solution; and measurement of volume or pressure change, which is suitable for reactions that produce or consume a gas.

7.4 Factors Affecting Reaction Rate: Concentration, Temperature and Surface Area

Four main factors affect how fast a reaction proceeds. Increasing the concentration of a reactant increases the number of particles present in a given



volume, raising the frequency of collisions between reactant particles and therefore increasing the rate; this is the basis of the law of mass action, which states that the rate of a reaction is proportional to the active masses (concentrations) of the reacting substances. For gaseous reactants, increasing pressure has an equivalent effect, since it increases the effective concentration of gas molecules in a given volume.

Raising the temperature increases reaction rate far more than a simple increase in collision frequency alone would predict; as a rough rule of thumb, reaction rate roughly doubles or triples for every 10 degrees C rise in temperature. The Maxwell-Boltzmann distribution explains why: raising the temperature shifts the distribution of molecular kinetic energies to higher values and broadens and flattens the curve, so that the area under the curve beyond the activation energy, representing the fraction of molecules with enough energy to react, increases sharply, far more than the modest increase in total collision frequency. Increasing the surface area of a solid reactant, for example by grinding a lump into a powder, exposes far more surface to the other reactant without changing the total amount of solid present, increasing the frequency of effective collisions at the solid's surface and therefore increasing rate.

7.5 Catalysis: Homogeneous and Heterogeneous Catalysts

A catalyst is a substance that increases the rate of a reaction without itself being permanently consumed, by providing an alternative reaction pathway, or mechanism, with a lower activation energy than the uncatalyzed route; because more collisions now have sufficient energy to follow this lower-energy pathway, the reaction proceeds faster, while the overall enthalpy change of the reaction, and the relative energies of reactants and products, remain unaffected. Familiar examples include platinum catalyzing the combination of hydrogen and oxygen to form water, manganese dioxide catalyzing the decomposition of potassium chlorate, and copper(II) chloride catalyzing the oxidation of hydrogen chloride to chlorine.

In homogeneous catalysis, the catalyst exists in the same phase as the reactants, as when nitrogen oxide gas catalyzes the gas-phase oxidation of sulfur dioxide to sulfur trioxide in the contact process, or when hydrogen ions catalyze the hydrolysis of an ester in aqueous solution. In heterogeneous catalysis, the



catalyst exists in a different phase from the reactants, most commonly a solid catalyst acting on gaseous or liquid reactants, as when platinum gauze catalyzes the industrial oxidation of ammonia to nitric oxide, or when finely divided nickel, palladium, or platinum catalyzes the hydrogenation of an alkene such as ethene to ethane. Enzymes are highly specific biological catalysts that speed up the biochemical reactions of living cells, and vitamins such as vitamin K often act as coenzymes, small molecules that assist an enzyme's catalytic action, in this case in the blood-clotting process.

7.6 Rate Law, Rate Constant and Order of Reaction

For a general reaction $aA + bB \rightarrow \text{products}$, the rate law, or rate equation, is the experimentally determined relationship $\text{Rate} = k[A]^x[B]^y$, where k is the specific rate constant of the reaction, and x and y are the orders of reaction with respect to A and B ; crucially, x and y must be found from experimental data and are not necessarily equal to the stoichiometric coefficients a and b in the balanced equation, because the rate law depends on the reaction's mechanism, not simply on its overall stoichiometry. The rate constant, k , is numerically equal to the rate of the reaction when every reactant concentration in the rate law is unity (1 mol dm^{-3}); its value depends on temperature and on whether a catalyst is present, but does not itself depend on the concentrations of the reactants.

The order of reaction with respect to a particular reactant is the power to which that reactant's concentration is raised in the experimentally determined rate law, and the overall order of the reaction is the sum of all the individual orders. For example, the oxidation of nitric oxide by ozone, $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, follows the rate law $\text{Rate} = k[\text{NO}][\text{O}_3]$, making it first order in NO , first order in O_3 , and second order overall; the reaction $2\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ follows $\text{Rate} = k[\text{H}_2][\text{NO}]^2$, making it first order in H_2 , second order in NO , and third order overall.

7.7 Types of Reaction Order

A zero order reaction has a rate that is independent of the concentration of its reactant(s), $\text{Rate} = k[A]^0 = k$, so changing the reactant concentration has no effect on rate; this occurs in some photochemical reactions, such as the sunlight-initiated reaction of hydrogen with chlorine to form hydrogen chloride, and in



certain catalyst-surface reactions, such as the decomposition of ammonia on a hot catalyst surface, where the rate is instead limited by the fixed number of active sites available. A first order reaction has a rate law in which the sum of the concentration exponents is 1, as in the decomposition of dinitrogen pentoxide, $2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$, which follows $\text{Rate} = k[\text{N}_2\text{O}_5]^1$.

A second order reaction has a rate law in which the sum of the exponents is 2, either from a single reactant squared, $\text{Rate} = k[\text{A}]^2$, or from two reactants each raised to the first power, $\text{Rate} = k[\text{A}][\text{B}]$, as in the oxidation of nitric oxide by ozone described above. A third order reaction has a rate law in which the sum of the exponents is 3, as in the reaction between iron(III) chloride and potassium iodide, which experimentally follows $\text{Rate} = k[\text{FeCl}_3][\text{KI}]^2$ despite involving eight reactant molecules in its balanced equation, and in the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, which follows $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$. A fractional order reaction has a rate law in which the sum of the exponents is not a whole number, as in the reaction of chloroform with chlorine to form carbon tetrachloride, $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$, which follows $\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$, an overall order of 1.5; fractional orders occur frequently in reactions that proceed through free-radical mechanisms.

7.8 Units of the Rate Constant

Because rate is always measured in $\text{mol dm}^{-3} \text{s}^{-1}$ while the concentration terms in a rate law are raised to different overall powers for reactions of different orders, the units of the rate constant, k , must themselves change with the order of the reaction to keep the rate law dimensionally consistent. Starting from $\text{Rate} = k[\text{Reactants}]^n$, rearranging gives $k^n = (\text{mol dm}^{-3})^{(1-n)} \text{s}^{-1}$, a general formula that can be used to find the units of k for any order n .

For a zero order reaction ($n = 0$), k_0 has units of $\text{mol dm}^{-3} \text{s}^{-1}$, the same units as rate itself. For a first order reaction ($n = 1$), the concentration term cancels entirely, leaving k_1 with units of s^{-1} . For a second order reaction ($n = 2$), k_2 has units of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, and for a third order reaction ($n = 3$), k_3 has units of $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$. Because each order of reaction corresponds to a distinct set of units for k , the units of an experimentally measured rate constant can themselves be used to identify the order of an otherwise unknown reaction.



7.9 Determination of the Rate Constant: Initial Rate and Half-Life Methods

The rate constant of a reaction can be calculated experimentally using two main methods. In the initial concentration (initial rate) method, several experiments are carried out using different known initial concentrations of the reactants, and the initial rate of each is measured; once the rate law has been established from how the initial rate changes between experiments, the measured rate and concentrations from any one experiment can be substituted into the rearranged rate law to solve for k . For example, for the reaction of hydrogen peroxide with iodide ions in acid, whose rate law is $\text{Rate} = k[\text{H}_2\text{O}_2]/[\text{I}^-]$, substituting an initial rate of $3.50 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ with $[\text{H}_2\text{O}_2] = 0.0200 \text{ mol dm}^{-3}$ and $[\text{I}^-] = 0.0100 \text{ mol dm}^{-3}$ gives $k = 1.75 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The half-life method applies specifically to first order reactions, and relies on the fact that a first order reaction's half-life, $t_{1/2}$, the time taken for a reactant's concentration to fall to half its original value, is a constant that does not depend on the starting concentration; this gives the direct relationship $k = 0.693 / t_{1/2}$. For example, a sample of hydrogen peroxide that decomposes by a first order process with a half-life of 2 hours, or 7200 seconds, has a rate constant $k = 0.693 / 7200 = 9.6 \times 10^{-5} \text{ s}^{-1}$; similarly, the first order conversion of cyclopropane to propene, with a half-life of 17.0 minutes (1020 seconds), has a rate constant $k = 0.693 / 1020$, approximately $6.8 \times 10^{-4} \text{ s}^{-1}$.

7.10 Reaction Mechanism, Molecularity and Intermediates

The overall balanced equation of a reaction shows only the starting reactants and final products, but many reactions do not occur in a single step; instead they proceed through a reaction mechanism, a sequence of elementary steps, each representing a single molecular event such as the breaking or forming of a bond, that together add up to the overall reaction. The molecularity of an elementary step is the number of reactant particles, atoms, ions, or molecules, that come together and react in that single step. A unimolecular step involves a single reactant molecule, as in the decomposition of $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$; a bimolecular step involves two colliding species, as in $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ or $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$; and a termolecular step, involving the simultaneous collision of three species, is rare because the probability of



three particles colliding together with the correct energy and orientation at the same instant is much lower than for a two-body collision, as in the stratospheric reaction $2\text{O}_2(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_3(\text{g}) + \text{O}_2(\text{g})$.

Intermediates are species, often ions or free radicals, that are produced in one step of a mechanism and completely consumed in a later step; because they are formed and then used up within the sequence of elementary steps, intermediates never appear in the overall balanced equation, which only shows what is left once every step has been added together.

7.11 The Rate-Determining Step

In many multi-step reaction mechanisms, one elementary step is significantly slower than all the others; this step, called the rate-determining step, controls the rate of the overall reaction in the same way that the narrowest point of a pipe limits the overall flow of water through it, regardless of how wide the rest of the pipe is. Because any step occurring after the rate-determining step cannot make the reaction go any faster than the rate-determining step already allows, species that only appear in steps after the rate-determining step do not appear in the experimentally observed rate law, while every species involved in, or before, the rate-determining step does appear in it; this means the order of a reaction can, in principle, be deduced directly from the molecularity of its rate-determining step.

For the reaction $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$, experiments show that doubling $[\text{H}_2]$ doubles the rate while doubling $[\text{NO}]$ quadruples the rate, giving the rate law $\text{Rate} = k[\text{H}_2][\text{NO}]^2$, first order in H_2 , second order in NO , third order overall; this matches a proposed two-step mechanism in which step 1, $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}_2$ (slow, rate-determining), is followed by step 2, $\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}$ (fast). Similarly, for the reaction $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}(\text{g})$, the experimentally observed rate law, $\text{Rate} = k[\text{NO}_2][\text{F}_2]$, first order in each reactant, matches a mechanism whose first, slow step, $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ (a fluorine atom), is rate-determining, while the second, fast step, $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$, does not affect the overall rate because the fluorine atoms produced in step 1 react almost as soon as they form.



Important Definitions

What is the rate of a reaction?

The change in the concentration of a reactant or product per unit time, $\text{Rate} = \Delta x / \Delta t$, usually expressed in $\text{mol dm}^{-3} \text{s}^{-1}$.

What is activation energy (E_a)?

The minimum energy that colliding reactant particles must together possess for a collision to be effective and lead to a reaction.

What is collision theory?

The theory that a reaction occurs only when reactant particles collide with the correct orientation and with at least the activation energy.

What is a rate law (rate equation)?

An experimentally determined equation, $\text{Rate} = k[A]^x[B]^y$, relating the rate of a reaction to the concentrations of its reactants.

What is the rate constant (k)?

The proportionality constant in the rate law, numerically equal to the rate of reaction when every reactant concentration is unity; it depends on temperature but not on concentration.

What is the order of a reaction?

The sum of the powers to which reactant concentrations are raised in the experimentally determined rate law.

What is molecularity?

The number of reactant particles, atoms, ions, or molecules, that collide and react together in a single elementary step of a mechanism.

What is a reaction intermediate?

A short-lived species, often an ion or free radical, produced in one step of a mechanism and consumed in a later step, so it does not appear in the overall equation.

What is the rate-determining step?

The slowest elementary step of a multi-step mechanism, which controls the rate of the overall reaction.

What is half-life ($t_{1/2}$)?



The time taken for the concentration of a reactant to fall to half of its original value.

Key Facts and Relations

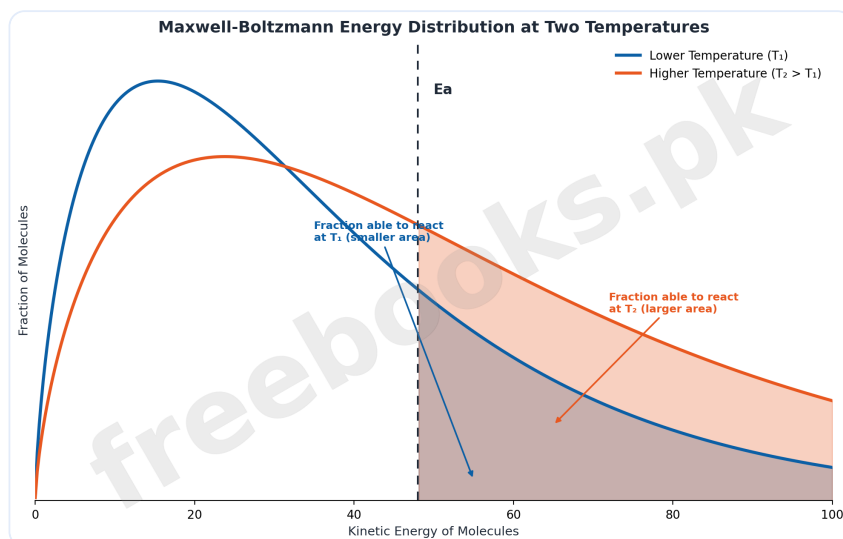
Topic	Key Fact / Relation
Rate of reaction	$\text{Rate} = \Delta x / \Delta t \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$
General rate law	$\text{Rate} = k[A]^x[B]^y$
Order of reaction	$n = x + y$ (sum of exponents in the rate law)
General units of rate constant	$k_n = (\text{mol dm}^{-3})^{(1-n)} \text{ s}^{-1}$
Zero order rate constant units	$k_0 = \text{mol dm}^{-3} \text{ s}^{-1}$
First order rate constant units	$k_1 = \text{s}^{-1}$
Second order rate constant units	$k_2 = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Third order rate constant units	$k_3 = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
Half-life relation (first order only)	$k = 0.693 / t_{1/2}$
Rate-determining step	Order of reaction = molecularity of the rate-determining step

Diagrams

Maxwell-Boltzmann Energy Distribution at Two Temperatures: A

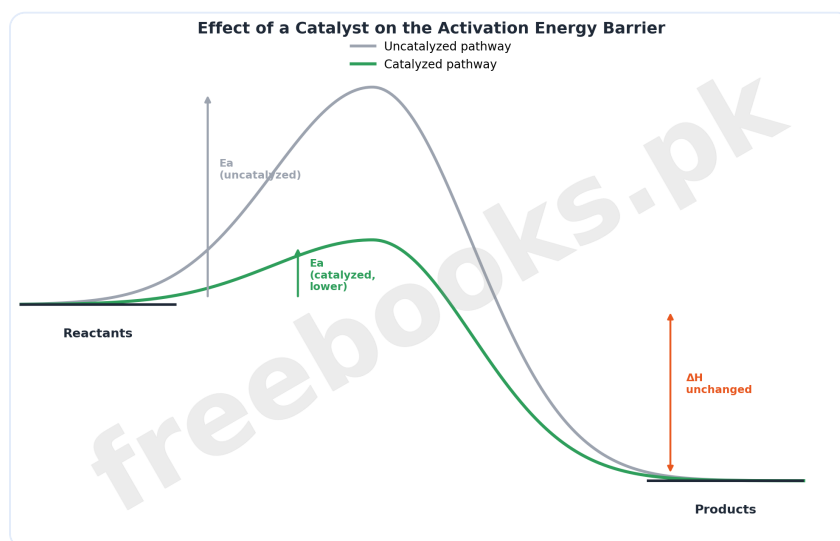
comparison of the distribution of molecular kinetic energies at a lower and a higher temperature, showing how the area under the curve beyond the activation energy (E_a), representing the fraction of molecules able to react, increases sharply as temperature rises





Maxwell-Boltzmann Energy Distribution at Two Temperatures

Effect of a Catalyst on the Activation Energy Barrier: An energy profile diagram comparing the catalyzed and uncatalyzed pathways of the same reaction, showing that a catalyst lowers the activation energy without changing the relative energies of reactants and products

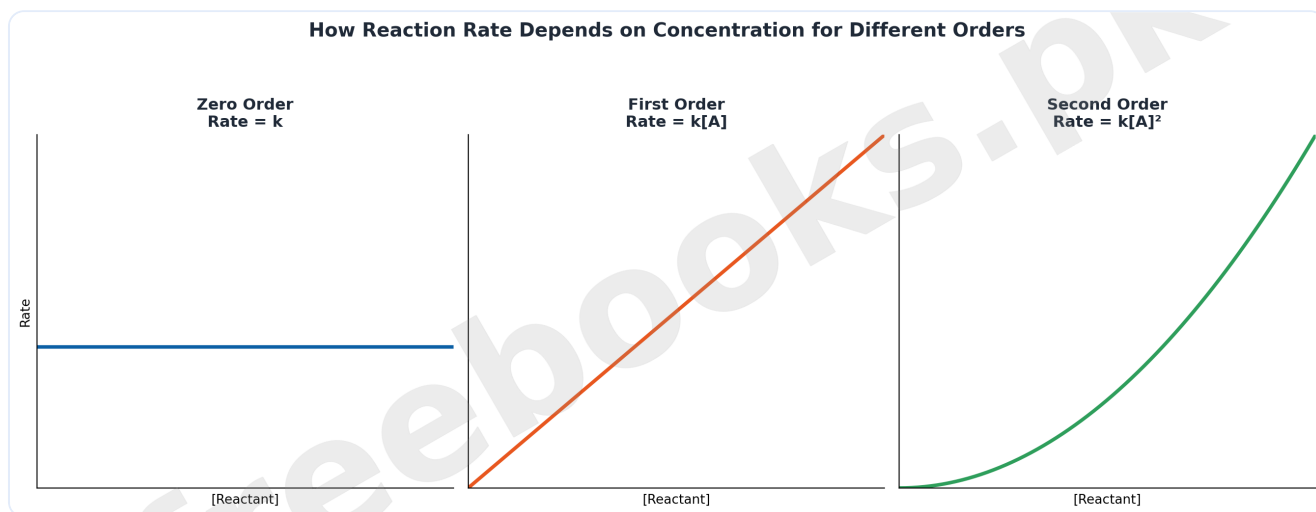


Effect of a Catalyst on the Activation Energy Barrier

How Reaction Rate Depends on Concentration for Different Orders:

Three graphs of rate against reactant concentration for zero order (constant rate), first order (rate directly proportional to concentration), and second order (rate proportional to the square of concentration) reactions





How Reaction Rate Depends on Concentration for Different Orders

Short Questions & Answers

Why do reactions such as the precipitation of silver chloride, the hydrolysis of an ester, and the rusting of iron proceed at such different rates?

These reactions have very different activation energies and involve very different reaction mechanisms; a low activation energy, ionic precipitation reaction like silver chloride formation needs almost no energy input to proceed, while a mechanism requiring bond-breaking and multiple steps, as in ester hydrolysis or the multi-stage oxidation involved in rusting, proceeds far more slowly because far fewer collisions are effective.

Why does only a small fraction of all molecular collisions actually result in a reaction?

For a collision to be effective, the colliding particles must have the correct orientation so the necessary bonds can break and form, and must together possess at least the activation energy; most collisions fail to meet one or both conditions, so only a small proportion of the total number of collisions occurring each second actually leads to a reaction.

Why is a graphical, tangent-slope method needed to find the instantaneous rate of a reaction?

A concentration-time graph for a reaction is curved, not a straight line, because the rate of reaction itself changes continuously as reactant is consumed; only the slope of a tangent drawn at a specific point on the curve gives the true



instantaneous rate at that moment, whereas the overall average rate would blur together the faster and slower parts of the reaction.

Why is $[H^+]$ left out of the rate law for the reaction between hydrogen peroxide and iodide ions, even though H^+ appears in the balanced equation?

Experiments show that changing the concentration of H^+ has no measurable effect on the rate of this reaction, meaning the reaction is zero order with respect to H^+ ; since the rate law only includes concentration terms for species whose concentration actually affects the rate, H^+ does not appear in it despite being a reactant in the overall stoichiometric equation.

Why does raising the temperature increase reaction rate by more than the increase in collision frequency alone would predict?

The Maxwell-Boltzmann distribution shows that raising temperature not only increases the total number of collisions occurring per second, but also sharply increases the fraction of those collisions with energy equal to or greater than the activation energy; this second effect dominates, which is why reaction rate typically doubles or triples for only a 10 degrees C rise in temperature.

Why can the rate law of a reaction not simply be read off from its balanced chemical equation?

The rate law depends on the actual reaction mechanism, specifically on the species involved in the rate-determining step, not on the overall stoichiometric coefficients of the balanced equation; because most reactions proceed through several elementary steps rather than a single collision matching the overall equation, the orders in the rate law must be determined experimentally.

Why is the half-life method for finding a rate constant only straightforwardly applicable to first order reactions?

For a first order reaction, the half-life is a genuine constant, independent of the starting concentration, so a single measured half-life can be substituted directly into $k = 0.693/t_{1/2}$; for reactions of other orders, the half-life itself depends on the initial concentration, so a single half-life value is not sufficient on its own to calculate the rate constant.

Why is a termolecular elementary step much rarer than a unimolecular or bimolecular step?



A termolecular step requires three separate reactant particles to collide simultaneously with both the correct orientation and sufficient combined energy; the probability of three independent particles meeting these conditions all at the same instant is far lower than for a two-body collision, so most reaction mechanisms proceed through a series of unimolecular and bimolecular steps instead.

Why do reaction intermediates never appear in the overall balanced equation of a reaction?

An intermediate is generated in one elementary step of the mechanism and then completely used up in a later step; when all the elementary steps of the mechanism are added together to give the overall reaction, the intermediate is produced and consumed in equal amounts, so it cancels out and does not appear among the final reactants or products.

Why does the order of a reaction sometimes match the molecularity of its proposed rate-determining step but not the overall balanced equation?

The rate-determining step is the single elementary step that limits how fast the whole reaction can proceed, so the species and their powers in the experimentally observed rate law reflect only the species involved in, or before, that one step; the overall balanced equation, by contrast, is simply the sum of every step in the mechanism and gives no information about which step is slowest.

Long Questions & Answers

Explain how collision theory accounts for the rate of a chemical reaction, and describe how concentration, temperature, surface area and catalysts each affect that rate.

What conditions must be satisfied for a collision between reactant particles to result in a reaction?

The colliding particles must be oriented correctly relative to one another, so that the bonds that need to break and form are actually able to do so, and together they must possess at least the activation energy needed to reach the transition



state; a collision lacking either the correct orientation or sufficient energy is ineffective and does not lead to a reaction.

How does increasing reactant concentration increase reaction rate?

According to the law of mass action, rate is proportional to the active masses, or concentrations, of the reacting substances; increasing concentration packs more particles into the same volume, which raises the frequency of collisions between reactant particles and therefore increases the number of effective collisions occurring per unit time.

How does increasing temperature affect the fraction of molecules able to react?

Raising temperature shifts the Maxwell-Boltzmann distribution of molecular kinetic energies toward higher values and broadens and flattens the curve, so the area beyond the activation energy, representing the fraction of molecules with enough energy to react, increases sharply; this effect, rather than the modest rise in total collision frequency, is why reaction rate typically doubles or triples for every 10 degrees C increase in temperature.

Why does increasing the surface area of a solid reactant increase reaction rate?

Grinding a solid into smaller pieces or a fine powder exposes far more of its surface to the other reactant without changing the total amount of solid present; because reaction can only occur at the exposed surface, this greatly increases the frequency of effective collisions at the solid-reactant interface and therefore increases rate.

How does a catalyst increase reaction rate without being permanently consumed?

A catalyst provides an alternative reaction pathway, or mechanism, with a lower activation energy than the uncatalyzed route, so a larger fraction of collisions now have enough energy to react via this new pathway; because the catalyst takes part in an early step of this alternative mechanism but is regenerated in a



later step, it re-emerges chemically unchanged at the end and does not appear in the overall stoichiometric equation.

Describe how the rate law, rate constant and order of a reaction are determined experimentally, and explain the role of the rate-determining step in a reaction mechanism.

What is a rate law, and how does it differ from the balanced chemical equation of a reaction?

A rate law, $\text{Rate} = k[\text{A}]^x[\text{B}]^y$, is an experimentally determined relationship between the rate of a reaction and the concentrations of its reactants; unlike the coefficients in a balanced chemical equation, the exponents x and y must be measured rather than assumed, because the rate law reflects the reaction's actual mechanism, not simply its overall stoichiometry.

How can the initial concentration method be used to determine a reaction's rate constant?

Several experiments are carried out using different known initial concentrations of the reactants, and the initial rate of each experiment is measured; comparing how the initial rate changes as each concentration is varied reveals the order with respect to that reactant, and once the full rate law is known, the measured rate and concentrations from any one experiment can be substituted into the rearranged rate law to solve for the rate constant, k .

How does the half-life method give the rate constant of a first order reaction?

The time taken for the reactant's concentration to fall to half its original value, the half-life, is measured experimentally; because a first order reaction's half-life is a constant that does not depend on the starting concentration, the rate constant can be found directly from $k = 0.693/t_{1/2}$ without needing any further concentration data.



What is meant by the rate-determining step of a reaction mechanism?

It is the slowest of the elementary steps that together make up a multi-step reaction mechanism; because this step acts as a bottleneck, comparable to the narrowest point of a pipe limiting the overall flow of water through it, it controls the rate of the entire reaction regardless of how fast the other steps are.

How can the identity of the rate-determining step be confirmed using the experimentally observed rate law?

A proposed mechanism is only considered valid if the species and their powers in its rate-determining step reproduce the rate law actually measured in the laboratory; if the rate-determining step's molecularity does not match the experimentally observed orders of reaction, the proposed mechanism must be rejected or revised.

Multiple Choice Questions (MCQs)

As a reaction proceeds and its reactants are gradually consumed, the rate of reaction typically:

- A. Increases steadily throughout
- B. Decreases as the reaction proceeds
- C. Stays exactly constant at every order of reaction
- D. Increases sharply and then stops abruptly

Answer: B. Decreases as the reaction proceeds

Explanation: As reactant concentration falls, the frequency of effective collisions generally falls too, so rate decreases over the course of most reactions; a zero order reaction is the main exception, since its rate does not depend on concentration.

Raising the temperature of a reaction increases its rate mainly because:

- A. Activation energy increases with temperature
- B. Activation energy decreases with temperature
- C. Both the frequency and the energy of effective collisions increase
- D. Only the total number of collisions increases, not their energy

Answer: C. Both the frequency and the energy of effective collisions increase

Explanation: The Maxwell-Boltzmann distribution shows that a higher



temperature increases both the overall collision frequency and, more significantly, the fraction of collisions with energy at or above the activation energy.

Comparing two reactions at the same temperature, the one with the lower activation energy will have:

- A. A smaller rate constant
- B. A larger rate constant
- C. Exactly the same rate constant
- D. A rate constant that depends only on enthalpy change

Answer: B. A larger rate constant

Explanation: A lower activation energy means a larger fraction of collisions possess enough energy to react at a given temperature, giving that reaction a larger rate constant.

A reaction whose rate does not change when the concentration of a particular reactant is changed is:

- A. Second order with respect to that reactant
- B. First order with respect to that reactant
- C. Zero order with respect to that reactant
- D. Impossible to classify by order

Answer: C. Zero order with respect to that reactant

Explanation: Zero order with respect to a reactant means that reactant's concentration term has an exponent of 0 in the rate law, so changing its concentration has no effect on the measured rate.

On a Maxwell-Boltzmann distribution curve, the shaded area beyond the activation energy represents:

- A. The total number of molecules in the sample
- B. The fraction of molecules with enough energy to react
- C. The average kinetic energy of all the molecules
- D. The value of the rate constant

Answer: B. The fraction of molecules with enough energy to react

Explanation: The area under the curve beyond E_a corresponds to the proportion of molecules that possess at least the minimum energy needed for an effective collision.



If doubling the concentration of a reactant causes the reaction rate to increase four-fold, the reaction is:

- A. Zero order with respect to that reactant
- B. First order with respect to that reactant
- C. Second order with respect to that reactant
- D. Third order with respect to that reactant

Answer: C. Second order with respect to that reactant

Explanation: Doubling the concentration raised the rate by a factor of $2^2 = 4$, so the exponent, and therefore the order, with respect to that reactant is 2.

In a multi-step reaction mechanism, the rate-determining step is:

- A. Always the first step written in the mechanism
- B. Always the final step of the mechanism
- C. The slowest of the elementary steps
- D. The fastest of the elementary steps

Answer: C. The slowest of the elementary steps

Explanation: Whichever elementary step happens to be slowest acts as the bottleneck and limits the overall rate of the reaction, regardless of its position within the mechanism.

The units of a reaction's rate constant, k , depend primarily on:

- A. The activation energy of the reaction
- B. The temperature at which the reaction is carried out
- C. The overall order of the reaction
- D. The stoichiometric coefficients of the balanced equation

Answer: C. The overall order of the reaction

Explanation: Because $k_n = (\text{mol dm}^{-3})^{(1-n)} \text{ s}^{-1}$, the units of k are determined entirely by n , the overall order of the reaction, not by activation energy, temperature, or stoichiometric coefficients.

A first order reaction has a half-life of 20 minutes. Its rate constant is closest to:

- A. 0.05 min^{-1}
- B. 0.0173 min^{-1}
- C. 0.0347 min^{-1}
- D. 13.86 min^{-1}



Answer: C. 0.0347 min^{-1}

Explanation: Using $k = 0.693/t_{1/2} = 0.693/20 \text{ minutes}$ gives $k = 0.0347 \text{ min}^{-1}$.

On an energy profile diagram, the effect of adding a catalyst is shown as:

- A. A higher activation-energy peak
- B. A lower activation-energy peak, with reactant and product energy levels unchanged
- C. A change in the enthalpy of the reactants
- D. A shift in the position of chemical equilibrium

Answer: B. A lower activation-energy peak, with reactant and product energy levels unchanged

Explanation: A catalyst provides an alternative pathway with a lower activation energy; it does not alter the relative energies of reactants and products, so the overall enthalpy change of the reaction is unaffected.

Quick Revision Summary

- Collision theory: a reaction occurs only when particles collide with the correct orientation and with at least the activation energy (E_a)
- Rate of reaction = $\Delta x / \Delta t$, units $\text{mol dm}^{-3} \text{ s}^{-1}$; instantaneous rate = slope of tangent on a concentration-time graph, distinct from average rate
- Concentration measured chemically (titration, discontinuous data) or physically (spectrophotometry, conductivity, volume/pressure change; continuous data)
- Rate increases with concentration (law of mass action), temperature (Maxwell-Boltzmann distribution), surface area, and presence of a catalyst
- Catalysts lower E_a via an alternative pathway without being consumed; homogeneous catalysis (same phase) vs heterogeneous catalysis (different phase)
- Rate law: $\text{Rate} = k[A]^x[B]^y$; x and y are found experimentally, not read off the balanced equation's coefficients
- Order of reaction = sum of exponents in the rate law; can be zero, first, second, third, or fractional
- Units of rate constant: $k_n = (\text{mol dm}^{-3})^{(1-n)} \text{ s}^{-1}$; $k_0 = \text{mol dm}^{-3} \text{ s}^{-1}$, $k_1 = \text{s}^{-1}$, $k_2 = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_3 = \text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$



- Rate constant found via the initial concentration method (multiple experiments, rearranged rate law) or the half-life method (first order only, $k = 0.693/t_{1/2}$)
- Reaction mechanism = sequence of elementary steps; molecularity = number of species colliding in one step (unimolecular, bimolecular, termolecular)
- Intermediates form in one step and are consumed in a later step; they never appear in the overall balanced equation
- Rate-determining step = the slowest elementary step; controls the overall rate; species only appearing after it do not appear in the rate law
- Order of reaction can often be deduced directly from the molecularity of the proposed rate-determining step

Exam Tips

- When identifying reaction order from experimental data, check exactly how the rate changes when one concentration is doubled while the others are held constant, rather than assuming order matches the stoichiometric coefficients
- Always convert time values to seconds before substituting into $k = 0.693/t_{1/2}$ if the rate constant is required in s^{-1}
- State the units alongside any calculated rate constant, since those units change with the order of the reaction and are themselves a clue to identifying an unknown order
- When proposing a reaction mechanism, check that the elementary steps sum to the correct overall balanced equation and that the rate-determining step reproduces the experimentally observed rate law
- Do not confuse molecularity (the number of species in one elementary step, always a whole number) with order of reaction (found experimentally, and can be zero, fractional, or otherwise unrelated to any single step's molecularity)
- Keep concentration and rate units consistent throughout a calculation, $mol\ dm^{-3}$ for concentration and $mol\ dm^{-3}\ s^{-1}$ for rate, so that the units of k obtained match the reaction's order



Chapter 8: Chemical Equilibrium

Chemical equilibrium describes the state reached by a reversible reaction, one that proceeds in both the forward and reverse directions rather than going to completion, when it is carried out in a closed container: the concentrations of reactants and products stop changing, and the rate of the forward reaction becomes exactly equal to the rate of the reverse reaction. Although the system appears static from the outside, at the molecular level both reactions continue indefinitely at equal rates, which is why this state is called a dynamic, rather than a static, equilibrium; the same idea applies to purely physical changes, such as the equilibrium between a liquid and its vapour in a closed container.

The chapter introduces the equilibrium constant, K_c , which measures the position of an equilibrium under a given set of conditions and depends only on temperature, and shows how it can equivalently be expressed in terms of partial pressures (K_p), moles (K_n), or mole fractions (K_x). It then applies Le Chatelier's principle, that a system at equilibrium responds to any imposed change by shifting to counteract that change, to predict how altering concentration, pressure, volume, or temperature shifts the position of an equilibrium, and closes by using these ideas to explain how industrial processes such as the Haber process and the contact process are optimized to maximize product yield.

Learning Objectives

- Distinguish between macroscopic events, observable with the naked eye, and microscopic events, occurring at the molecular level, in a chemical system approaching equilibrium
- Describe a reversible reaction and define dynamic chemical equilibrium in terms of equal forward and reverse rates and constant reactant/product concentrations
- Define dynamic equilibrium between two physical states, such as a liquid and its vapour, or a solid and its liquid
- State the necessary conditions for chemical equilibrium and describe the characteristic features by which it can be recognized



- Deduce the equilibrium constant expression, K_c , for a homogeneous reaction from its balanced chemical equation
- Write equilibrium expressions in terms of concentration (K_c), partial pressure (K_p), number of moles (K_n), and mole fraction (K_x), and relate these constants to one another
- Distinguish between homogeneous equilibria, where all species share one phase, and heterogeneous equilibria, where more than one phase is present
- State Le Chatelier's principle and apply it to predict the effect of changes in concentration, pressure, volume, temperature, or catalyst on a system at equilibrium
- Determine whether K_c increases or decreases with a change in temperature, given whether a reaction is exothermic or endothermic
- Explain how Le Chatelier's principle is applied industrially in the Haber process and the contact process to maximize product yield

Key Concepts

8.1 Reversible Reactions and Chemical Equilibrium

Reactions in which the reactants are completely consumed and converted into products are called irreversible reactions; such reactions stop once the limiting reactant is used up. Reversible reactions, by contrast, proceed continuously in both the forward and reverse directions without the concentrations of reactants and products ever falling to zero, and are written with a double arrow, such as $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, and $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. When a reversible reaction takes place in a closed container, so that none of the reacting substances can escape, the reaction eventually reaches a stage called chemical equilibrium, at which the concentrations of all reactants and products become constant and the rates of the forward and reverse reactions become equal.

8.2 Macroscopic and Microscopic Events; Dynamic Equilibrium

Macroscopic events are phenomena that can be observed with the naked eye without considering individual particles, such as a change in colour, the evolution or absorption of heat, the formation of a precipitate, the evolution of a gas, or a change in volume, pressure, or composition. Microscopic events, by contrast,



cannot be observed directly and include collisions between molecules, the breaking and forming of bonds, the rearrangement of atoms, and the loss or gain of electrons; macroscopic changes are simply the combined, observable result of huge numbers of simultaneous microscopic events.

Consider steam and carbon monoxide reacting to form hydrogen and carbon dioxide, $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$: when the gases are first mixed, the maximum possible number of collisions between H_2O and CO molecules occurs, so the forward reaction proceeds at its fastest rate, and this rate gradually slows as the reactants are consumed. At the same time, as H_2 and CO_2 molecules accumulate, collisions between them become more frequent, and the reverse reaction, which starts at a low rate, gradually speeds up. Eventually the forward and reverse rates become equal, and the reaction reaches chemical equilibrium; although the concentrations of reactants and products then stay constant, and the reaction may appear to have stopped, at the microscopic level both the forward and reverse reactions continue indefinitely at equal rates, making this a dynamic equilibrium rather than a static one.

8.3 Dynamic Equilibrium Between Two Physical States

Dynamic equilibrium also applies to purely physical changes: when a reversible phase change occurs, such as ice and water coexisting at 0 degrees C, water converts to ice at exactly the same rate that ice converts back to water, so no net change occurs even though both processes continue. A similar dynamic equilibrium exists between a liquid and its vapour in a closed container: molecules near the liquid's surface with enough energy escape into the gas phase, a process called evaporation, while gas-phase molecules that collide with the liquid surface are recaptured, a process called condensation.

As evaporation and condensation continue, their rates eventually become equal, establishing a dynamic equilibrium at which the vapour pressure remains constant at a given temperature as long as the system is undisturbed. Raising the temperature increases the average kinetic energy of the liquid's molecules, increasing both the rate of evaporation and, once more vapour is present, the rate of condensation, until a new dynamic equilibrium is reached at a higher equilibrium vapour pressure.



8.4 Conditions and Characteristics of Chemical Equilibrium

Chemical equilibrium can only be studied when two conditions are satisfied: the state of equilibrium applies only to reversible reactions, and equilibrium can only be established in a closed system, one from which no reactant or product is allowed to escape; a reversible reaction carried out in an open container never reaches equilibrium, since escaping gas continuously shifts the system in one direction. Several important characteristics follow from this: at equilibrium, the concentrations of reactants and products remain constant; the equilibrium state can be approached from either direction, starting from pure reactants or from pure products; a catalyst does not change the position of equilibrium or the value of the equilibrium constant, it only helps the system reach equilibrium more quickly; and the value of the equilibrium constant does not depend on the initial concentrations used, but depends only on temperature.

If pure solids or pure liquids take part in an equilibrium system, their concentrations are not included in the equilibrium constant expression, because the concentration of a pure solid or liquid, essentially its density, does not change and therefore has no effect on the value of the equilibrium constant.

8.5 Types of Equilibrium: Homogeneous and Heterogeneous

With respect to the physical states of the species involved, equilibria are classified into two types. A homogeneous equilibrium is one in which all reactants and products exist in the same phase, as in the synthesis of ammonia, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, the formation of sulfur trioxide, $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, or the esterification of ethanoic acid with ethanol, in which every species is a liquid. A heterogeneous equilibrium is one in which the reactants and products exist in more than one phase, as in the thermal decomposition of calcium carbonate, $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, the reaction of carbon with steam, $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$, or the reaction of iron with steam, $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$.

8.6 The Equilibrium Constant (K_c) and the Law of Mass Action

In 1864, the chemists Guldberg and Waage measured the compositions of many reaction systems at equilibrium and found that, for any reversible reaction, the



ratio of the product of the equilibrium concentrations of the products, each raised to its coefficient in the balanced equation, to the equivalent product of reactant concentrations, is always constant under a given set of conditions. For the general reaction $aA + bB \rightleftharpoons cC + dD$, this equilibrium constant expression is written $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, where square brackets denote molar concentration in mol dm^{-3} .

This expression can be derived from the law of mass action, which states that the rate of a reaction is proportional to the active masses (concentrations) of the reacting substances: for $A + B \rightleftharpoons C + D$, the forward rate is $k_f[A][B]$ and the reverse rate is $k_r[C][D]$, and since these two rates are equal at equilibrium, $k_f[A][B] = k_r[C][D]$, so $k_f/k_r = [C][D]/[A][B] = K_c$, a new constant called the equilibrium constant. Applying this to real reactions gives, for example, $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ for the synthesis of ammonia, and $K_c = \frac{[\text{NO}_2]^4[\text{O}_2]}{[\text{N}_2\text{O}_5]^2}$ for the decomposition of dinitrogen pentoxide; a worked example using equilibrium concentrations of $0.470 \text{ mol dm}^{-3}$ ethanoic acid, $0.070 \text{ mol dm}^{-3}$ ethanol, and $0.364 \text{ mol dm}^{-3}$ each of ethyl ethanoate and water gives $K_c = 4.03$ for the esterification reaction, while a propanone-hydrogen cyanide addition reaction with equilibrium concentrations of $0.0267 \text{ mol dm}^{-3}$ for each reactant and $0.0233 \text{ mol dm}^{-3}$ for the product gives $K_c = 32.7 \text{ dm}^3 \text{ mol}^{-1}$.

8.7 Units of K_c and Relationships Between Equilibrium Constants

When the total number of moles of reactants and products in the balanced equation are equal, the concentration units in the K_c expression cancel completely, leaving K_c with no units, as in the ester formation reaction; when the number of moles are unequal, as in ammonia synthesis, the units do not cancel, giving K_c units such as $\text{dm}^6 \text{ mol}^{-2}$ that depend on the specific reaction. Four different quantities can be used to express an equilibrium constant: K_c , based on molar concentrations; K_p , based on the partial pressures of gaseous species; K_n , based on numbers of moles; and K_x , based on mole fractions.

These four constants are related by $K_p = K_c(RT)^{\Delta n}$, $K_p = K_x(P)^{\Delta n}$, and $K_p = K_n(N)^{\Delta n}$, where R is the gas constant, T is the absolute temperature, P is the total pressure, N is the total number of moles present, and Δn is the difference between the number of moles of gaseous products and gaseous reactants in the balanced equation. If $\Delta n = 0$, meaning the



balanced equation has equal moles of gaseous reactants and products, then $K_p = K_c = K_x = K_n$, and the value of the equilibrium constant is the same regardless of which concentration units are used; a worked example converts $K_c = 6.0 \times 10^{-2}$ at 500 degrees C for ammonia synthesis ($\Delta n = -2$) into $K_p = 1.4 \times 10^{-5}$, showing that K_p is smaller than K_c for this reaction.

8.8 Le Chatelier's Principle

The position of equilibrium refers to the relative amounts of reactants and products present in an equilibrium mixture; if a system at equilibrium is disturbed so that the position shifts toward more product, the equilibrium is said to have shifted to the right, and if it shifts toward more reactant, it is said to have shifted to the left. Le Chatelier's principle, proposed by the French chemist Henry-Louis Le Chatelier, states that if a system at equilibrium is disturbed, it responds in such a way as to counteract, or partially nullify, the effect of that disturbance. This principle is most commonly applied to four types of disturbance: a change in concentration, a change in pressure or volume, a change in temperature, and the addition of a catalyst.

8.9 Effects of Concentration, Pressure/Volume and Catalyst on Equilibrium

Adding or removing a reactant or product disturbs an equilibrium, and the system shifts to partially counteract the change. This is illustrated by the reversible hydrolysis of bismuth(III) chloride, $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HCl}$: adding more BiCl_3 or water pushes the reaction forward, producing more BiOCl and HCl , while adding more BiOCl or HCl pushes the reaction in reverse, producing more BiCl_3 ; conversely, removing BiCl_3 shifts the reaction in reverse, and removing BiOCl or HCl shifts it forward. In every case, the equilibrium position changes, but the value of K_c itself remains constant, since K_c depends only on temperature.

A change in pressure or volume only affects the position of a gas-phase equilibrium when the number of moles of gaseous reactants differs from the number of moles of gaseous products; if these numbers are equal, changing pressure or volume has no effect on the equilibrium position. In the synthesis of ammonia, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, four moles of gaseous reactants form



two moles of gaseous product, so increasing the pressure, or decreasing the volume, shifts the equilibrium toward the side with fewer gas molecules, favouring the forward reaction and producing more ammonia; decreasing the pressure, or increasing the volume, shifts the equilibrium the other way, favouring the reactants.

A catalyst provides an alternative reaction pathway with a lower activation energy for both the forward and the reverse reaction equally, so it speeds up the rate at which equilibrium is reached without changing the equilibrium position or the value of the equilibrium constant; the overall yield of the reaction therefore stays the same, whether or not a catalyst is used, though a catalyst allows that same yield to be reached in far less time.

8.10 Effect of Temperature on Equilibrium

Temperature is the only factor that changes the actual numerical value of the equilibrium constant, K_c , rather than simply shifting the position of equilibrium while K_c stays fixed. For an exothermic reaction, such as $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, $\Delta H^\circ = -198 \text{ kJ}$, increasing the temperature favours the reverse, heat-absorbing reaction, shifting the equilibrium to the left, decreasing the concentration of SO_3 , and decreasing the value of K_c , which falls from about 1×10^{26} at 298 K to about 2.8×10^2 at 1000 K; decreasing the temperature has the opposite effect, favouring the forward reaction and increasing K_c , which is why SO_3 production is favoured at lower temperature.

For an endothermic reaction, such as $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, $\Delta H^\circ = +57.2 \text{ kJ}$, increasing the temperature favours the forward, heat-absorbing reaction, shifting the equilibrium to the right, increasing the concentration of NO_2 , and increasing the value of K_c , which rises from about 7.7×10^{-5} at 273 K to about 0.4 at 373 K; decreasing the temperature favours the reverse reaction and decreases K_c . In general, raising the temperature always favours whichever direction of a reaction is endothermic, regardless of whether that happens to be the forward or the reverse direction.



8.11 Industrial Applications: Haber's Process and the Contact Process

The synthesis of ammonia by the Haber process, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, $\Delta H = -46.11 \text{ kJ/mol}$, is exothermic and proceeds with a decrease in the number of gas moles, so Le Chatelier's principle predicts that maximum yield is favoured by continuously removing ammonia as it forms, by using high pressure, and by using low temperature. In practice, very low temperature makes the reaction far too slow to be economical, so industrial plants instead use a moderate temperature of around 673 K (400 degrees C) together with an iron catalyst, promoted with MgO, Al_2O_3 and SiO_2 , to speed up the approach to equilibrium, combined with a high pressure of 200 to 300 atmospheres; under these compromise conditions, useful yields of ammonia are obtained at a commercially practical rate, even though the very highest possible yield, up to 98.3 percent, would require far more extreme, and far less economical, conditions of very low temperature and very high (1000 atmosphere) pressure.

A similar compromise governs the production of sulfur trioxide in the contact process for making sulfuric acid, $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, $\Delta H = -97.9 \text{ kJ/mol}$: Le Chatelier's principle predicts that high pressure and low temperature favour the highest yield of SO_3 , but at low temperature the equilibrium is reached only very slowly. Industrially, a mixture of SO_2 and O_2 (as air) at about 1 atmosphere pressure is passed over a solid vanadium(V) oxide catalyst; because the reaction is exothermic, the gas temperature rises to around 600 degrees C as it reacts, so the mixture is cooled and recycled at the more favourable temperature of 400 to 500 degrees C to increase the final yield of SO_3 .

Important Definitions

What is a reversible reaction?

A reaction that proceeds continuously in both the forward and reverse directions, never going fully to completion, and is written with a double arrow ($\rightleftharpoons$).

What is an irreversible reaction?

A reaction in which the reactants are completely consumed and converted into products, stopping once the limiting reactant is used up.



What is chemical (dynamic) equilibrium?

The state of a reversible reaction in a closed system at which the concentrations of reactants and products are constant and the forward and reverse reaction rates are equal.

What are macroscopic events?

Observable phenomena, such as colour change, heat evolution, or precipitate formation, that occur without reference to individual particles.

What are microscopic events?

Molecular-level phenomena, such as collisions and the breaking or forming of bonds, that cannot be observed directly but underlie macroscopic change.

What is the equilibrium constant (K_c)?

The constant ratio of product concentrations to reactant concentrations, each raised to its stoichiometric coefficient, at equilibrium, for a given reaction at a given temperature.

What is the law of mass action?

The principle that the rate of a chemical reaction is proportional to the active masses (molar concentrations) of the reacting substances.

What is a homogeneous equilibrium?

An equilibrium system in which all reactants and products exist in the same physical phase.

What is a heterogeneous equilibrium?

An equilibrium system in which the reactants and products exist in more than one physical phase.

What is Le Chatelier's principle?

The principle that if a system at equilibrium is disturbed, it shifts in a way that counteracts, or partially nullifies, the effect of that disturbance.

Key Facts and Relations

Topic	Key Fact / Relation
General equilibrium constant expression	$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ for $aA + bB \rightleftharpoons cC + dD$



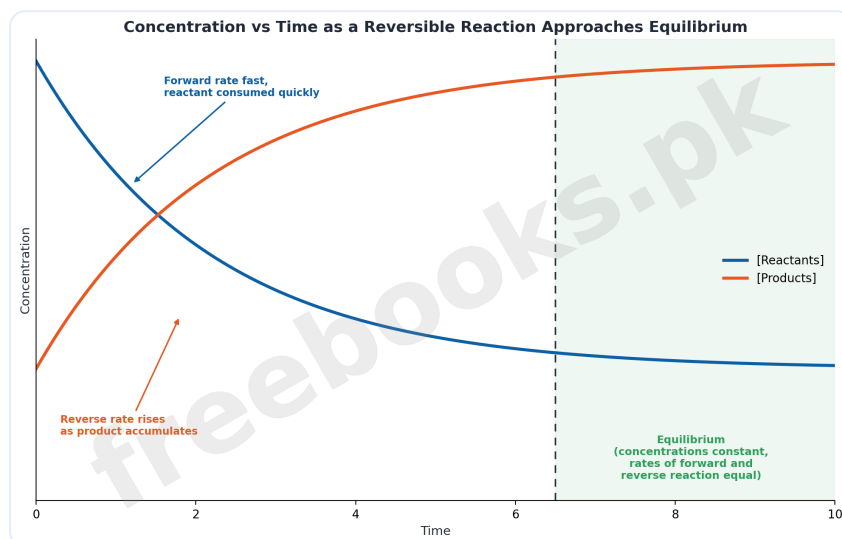
Topic	Key Fact / Relation
Equilibrium constant from rate constants	$K_c = k_f / k_r$
Partial pressure equilibrium constant	$K_p = (p_C^c \cdot p_D^d) / (p_A^a \cdot p_B^b)$
Relating K_p and K_c	$K_p = K_c (RT)^{\Delta n}$
Relating K_p and K_x	$K_p = K_x (P)^{\Delta n}$
Relating K_p and K_n	$K_p = K_n (N)^{\Delta n}$
Special case when $\Delta n = 0$	$K_p = K_c = K_x = K_n$
Le Chatelier's principle	A system at equilibrium shifts to counteract any imposed disturbance
Effect of pressure increase (unequal gas moles)	Equilibrium shifts toward the side with fewer moles of gas
Effect of temperature	Exothermic reaction: T up shifts equilibrium left, K_c decreases; Endothermic reaction: T up shifts equilibrium right, K_c increases

Diagrams

Concentration vs Time as a Reversible Reaction Approaches

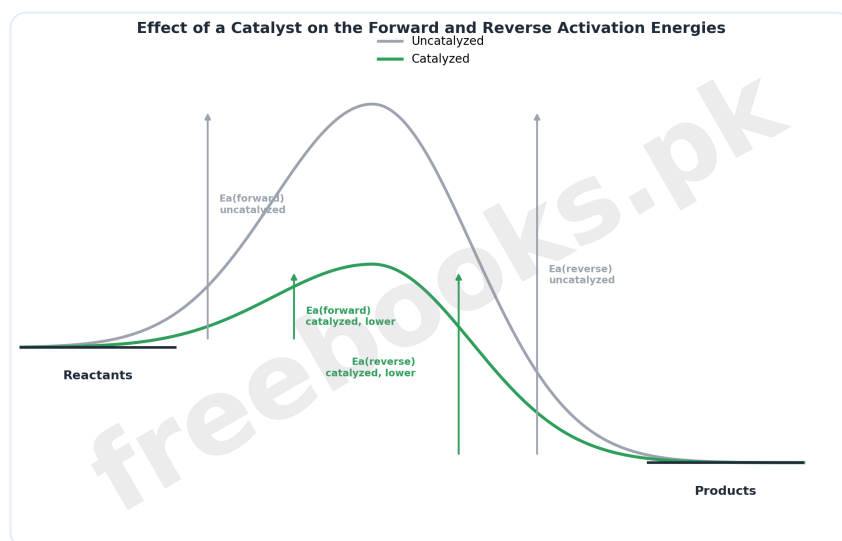
Equilibrium: A plot showing reactant concentration falling and product concentration rising as a reversible reaction proceeds, both becoming constant once the forward and reverse reaction rates become equal at equilibrium





Concentration vs Time as a Reversible Reaction Approaches Equilibrium

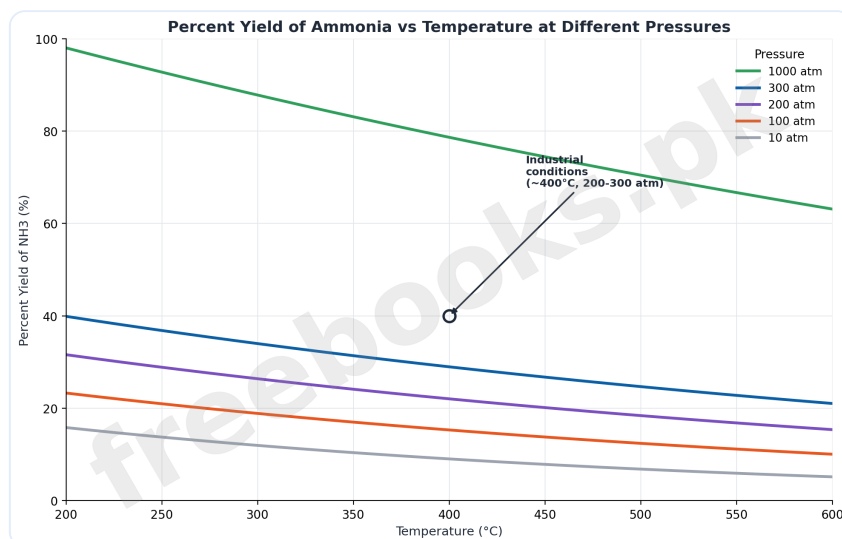
Effect of a Catalyst on the Forward and Reverse Activation Energies: An energy profile diagram showing that a catalyst lowers the activation energy of both the forward and reverse reactions by the same amount, speeding up the approach to equilibrium without changing its position



Effect of a Catalyst on the Forward and Reverse Activation Energies

Percent Yield of Ammonia vs Temperature at Different Pressures: A set of curves showing how the percentage yield of ammonia in the Haber process decreases with increasing temperature and increases with increasing pressure, with the industrial compromise conditions marked





Percent Yield of Ammonia vs Temperature at Different Pressures

Short Questions & Answers

Why is the equilibrium reached by a reversible reaction described as dynamic rather than static?

Although the concentrations of reactants and products stop changing at equilibrium, individual molecules never stop reacting; the forward and reverse reactions both continue indefinitely at the molecular level, but because they proceed at exactly equal rates, there is no net change in the bulk concentrations, making the equilibrium dynamic rather than static.

Why can chemical equilibrium only be established in a closed system?

Equilibrium requires the forward and reverse reactions to reach equal rates while none of the reacting substances escape; in an open system, a gaseous reactant or product can continuously leave the reaction vessel, preventing the concentrations from ever stabilizing and so preventing equilibrium from being established.

Why does a catalyst not change the position of equilibrium or the value of K_c ?

A catalyst lowers the activation energy of the forward and reverse reactions by the same amount, so it speeds up both reactions equally; because it accelerates the approach to equilibrium without favouring one direction over the other, the final equilibrium position, and therefore the value of K_c , remains unchanged.



Why are pure solids and pure liquids left out of the equilibrium constant expression?

The concentration of a pure solid or liquid, essentially its density, is a fixed physical property that does not change no matter how much of the solid or liquid is present; since it cannot vary, including it in the K_c expression would add nothing, so only species whose concentrations can actually change are included.

Why does the equilibrium constant K_c for the ester formation reaction have no units, while K_c for ammonia synthesis does?

In the ester formation reaction, the total number of moles of reactants equals the total number of moles of products, so every mol dm^{-3} unit in the numerator of the K_c expression is cancelled by an identical unit in the denominator; in ammonia synthesis, the moles of reactants and products are unequal, so the units do not fully cancel, leaving K_c with units such as $\text{dm}^6 \text{ mol}^{-2}$.

Why does increasing the pressure on the Haber process equilibrium shift it toward producing more ammonia?

Four moles of gaseous reactants form only two moles of gaseous product in this reaction, so the product side occupies a smaller volume at the same pressure and temperature; increasing the pressure disturbs the equilibrium, and by Le Chatelier's principle the system shifts toward the side with fewer gas molecules, the product side, to partially counteract the pressure increase.

Why does increasing temperature decrease the value of K_c for an exothermic reaction but increase it for an endothermic reaction?

Raising temperature always favours whichever direction of a reaction absorbs heat; for an exothermic reaction, this is the reverse direction, so the equilibrium shifts toward reactants and K_c falls, while for an endothermic reaction, this is the forward direction, so the equilibrium shifts toward products and K_c rises.

Why is a moderate rather than a very low temperature used industrially in the Haber process, even though the reaction is exothermic?

Although Le Chatelier's principle shows that low temperature favours a higher equilibrium yield of ammonia, at very low temperature the rate at which equilibrium is reached becomes far too slow to be commercially practical; a moderate temperature, combined with a catalyst, is used instead as a compromise that gives an acceptable yield within an economically reasonable time.



Why is the hot gas mixture cooled and recycled during the contact process for making sulfur trioxide?

The oxidation of SO_2 to SO_3 is exothermic, so the reacting gas mixture heats up to around 600 degrees C as it passes over the catalyst, a temperature at which the equilibrium yield of SO_3 is relatively low; cooling the mixture to 400-500 degrees C before recycling it shifts the equilibrium back toward a higher yield of SO_3 without needing to run the whole process at an uneconomically low temperature throughout.

Why does removing a product from an equilibrium mixture shift the reaction further toward that product?

Removing a product lowers its concentration below the equilibrium value, and by Le Chatelier's principle the system responds by shifting in the direction that replaces some of what was removed; since the forward reaction produces more of that product, the equilibrium shifts forward, converting more reactant into product until a new equilibrium position is established.

Long Questions & Answers

Explain the difference between macroscopic and microscopic events in a reversible reaction, and describe how the concept of dynamic equilibrium follows from this distinction.

What is the difference between a macroscopic and a microscopic event in a chemical system?

A macroscopic event is a change that can be observed directly with the naked eye, such as a colour change or the evolution of a gas, while a microscopic event is a molecular-level occurrence, such as a collision between particles or the breaking of a bond, that cannot be observed directly but is what actually causes the macroscopic change.

How does the rate of the forward reaction change as steam and carbon monoxide are first mixed?

At the moment of mixing, the concentrations of both reactants are at their highest, so the frequency of effective collisions between H_2O and CO molecules,



and therefore the rate of the forward reaction, is at its maximum; as the reactants are gradually consumed, this rate steadily decreases.

How does the rate of the reverse reaction change as the forward reaction proceeds?

At the start, essentially no product molecules are present, so the reverse reaction proceeds extremely slowly; as H_2 and CO_2 accumulate from the forward reaction, collisions between them become more frequent, so the rate of the reverse reaction gradually increases.

What happens once the forward and reverse rates become equal?

Once the two rates are equal, the amount of reactant being converted to product each second exactly balances the amount of product being converted back to reactant, so the concentrations of every species stop changing; the system has reached chemical equilibrium.

Why is this equilibrium described as dynamic rather than as the reaction having stopped?

Even though the bulk concentrations no longer change, individual reactant and product molecules are still continuously colliding and reacting in both directions at the microscopic level; the system only appears unchanging because these two ongoing processes occur at exactly equal rates, which is the defining feature of a dynamic, rather than a static, equilibrium.

State Le Chatelier's principle and explain how it is used to predict the effect of changes in concentration, pressure, and temperature on a system at equilibrium.

What does Le Chatelier's principle state?

It states that if a system at equilibrium is disturbed by an external change, the system responds in a way that counteracts, or partially nullifies, the effect of that disturbance, shifting the position of equilibrium until a new balance is established.



How does adding more of a reactant affect the position of equilibrium?

Adding more reactant increases its concentration above the equilibrium value, so the system shifts in the forward direction, consuming some of the added reactant and producing more product, until a new equilibrium position is established at which the rates of the forward and reverse reactions are again equal.

How does increasing the pressure on a gaseous equilibrium affect its position?

If the numbers of moles of gas differ between the reactant and product sides, increasing pressure shifts the equilibrium toward whichever side has fewer moles of gas, since that side occupies less volume and partially relieves the increased pressure; if the moles of gas are equal on both sides, changing pressure has no effect on the equilibrium position.

How does increasing the temperature affect an exothermic equilibrium differently from an endothermic one?

Because raising temperature always favours whichever direction of a reaction absorbs heat, increasing temperature shifts an exothermic reaction's equilibrium toward the reactants, decreasing K_c , while it shifts an endothermic reaction's equilibrium toward the products, increasing K_c .

Why is temperature different from concentration and pressure in how it affects equilibrium?

Changing concentration or pressure shifts the position of equilibrium while leaving the numerical value of the equilibrium constant unchanged, since K_c depends only on temperature; changing temperature, however, actually changes the value of K_c itself, which is why temperature is described as the only factor that alters the equilibrium constant rather than simply shifting the equilibrium position around a fixed K_c .

Multiple Choice Questions (MCQs)

A reaction that proceeds continuously in both directions without going to completion in a closed container is called:



- A. An irreversible reaction
- B. A reversible reaction
- C. A spontaneous reaction
- D. A catalyzed reaction

Answer: B. A reversible reaction

Explanation: A reversible reaction proceeds in both the forward and reverse directions simultaneously and is written with a double arrow; it never goes fully to completion in a closed system.

At chemical equilibrium, which of the following is true?

- A. The forward reaction has stopped completely
- B. The reverse reaction has stopped completely
- C. The forward and reverse reaction rates are equal
- D. The concentrations of reactants and products are always equal to each other

Answer: C. The forward and reverse reaction rates are equal

Explanation: Equilibrium is defined by the forward and reverse reaction rates becoming equal, not by either reaction stopping and not by the concentrations of reactants and products necessarily being equal to one another.

Why is chemical equilibrium impossible to establish in an open container?

- A. The reaction proceeds too quickly
- B. Reactants or products can escape, preventing concentrations from stabilizing
- C. Catalysts cannot function in open containers
- D. Open containers always favour the reverse reaction

Answer: B. Reactants or products can escape, preventing concentrations from stabilizing

Explanation: Equilibrium requires the concentrations of every species to stabilize; if a gaseous reactant or product can escape from an open container, the concentrations keep changing and equilibrium can never be reached.

Which of the following correctly gives the equilibrium constant expression for $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$?

- A. $K_c = [\text{CaO}][\text{CO}_2]/[\text{CaCO}_3]$
- B. $K_c = [\text{CO}_2]$
- C. $K_c = [\text{CaCO}_3]/[\text{CaO}][\text{CO}_2]$
- D. $K_c = [\text{CaO}]/[\text{CaCO}_3]$



Answer: B. $K_c = [\text{CO}_2]$

Explanation: Pure solids are left out of the equilibrium constant expression because their concentration does not change; only the gaseous CO_2 is included, giving $K_c = [\text{CO}_2]$.

For a reaction in which the total moles of gaseous reactants equal the total moles of gaseous products, which statement is correct?

- A. K_p is always larger than K_c
- B. K_p is always smaller than K_c
- C. K_p equals K_c
- D. K_p cannot be calculated

Answer: C. K_p equals K_c

Explanation: When $\Delta n = 0$, the relationship $K_p = K_c(RT)^{\Delta n}$ reduces to $K_p = K_c(RT)^0 = K_c$, so the two constants are equal.

Increasing the pressure on the equilibrium $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ shifts the position of equilibrium:

- A. To the left, favouring reactants
- B. To the right, favouring products
- C. It has no effect on this equilibrium
- D. It only affects the rate, not the position

Answer: B. To the right, favouring products

Explanation: Four moles of gaseous reactants form two moles of gaseous product in this reaction; increasing pressure shifts the equilibrium toward the side with fewer gas moles, the product side, favouring ammonia formation.

For the exothermic reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, increasing the temperature will:

- A. Increase the value of K_c
- B. Decrease the value of K_c
- C. Leave K_c unchanged but shift the position of equilibrium
- D. Have no effect on K_c or the position of equilibrium

Answer: B. Decrease the value of K_c

Explanation: Raising the temperature favours the endothermic, reverse direction of an exothermic reaction, shifting equilibrium toward reactants and decreasing the numerical value of K_c .

What effect does adding a catalyst have on a system at equilibrium?



- A. It shifts the equilibrium toward more product
- B. It shifts the equilibrium toward more reactant
- C. It increases the value of K_c
- D. It has no effect on the equilibrium position or K_c , but speeds up how quickly equilibrium is reached

Answer: D. It has no effect on the equilibrium position or K_c , but speeds up how quickly equilibrium is reached

Explanation: A catalyst lowers the activation energy of the forward and reverse reactions equally, so it speeds up the approach to equilibrium without changing the equilibrium position or the value of K_c .

In the industrial Haber process, a moderate temperature of about 400 degrees C is used, together with a catalyst, mainly because:

- A. Very low temperature would give the highest yield but make the reaction too slow to be economical
- B. High temperature always gives the highest yield of ammonia
- C. Temperature has no effect on the rate of ammonia synthesis
- D. The catalyst only works efficiently at high temperature

Answer: A. Very low temperature would give the highest yield but make the reaction too slow to be economical

Explanation: Although lower temperature favours a higher equilibrium yield for this exothermic reaction, at very low temperature the reaction becomes too slow to be commercially useful, so a moderate temperature with a catalyst is used as a practical compromise.

If the concentration of a product is decreased at equilibrium, the reaction will:

- A. Shift in the reverse direction
- B. Shift in the forward direction to replace the product
- C. Remain at the same equilibrium position
- D. Stop occurring entirely

Answer: B. Shift in the forward direction to replace the product

Explanation: By Le Chatelier's principle, removing product disturbs the equilibrium; the system responds by shifting in the forward direction, converting more reactant into product to partially replace what was removed.



Quick Revision Summary

- Reversible reaction: proceeds in both directions, written with a double arrow ($\rightleftharpoons$); irreversible reaction: goes to completion
- Chemical equilibrium: reached in a closed system when forward and reverse rates become equal and concentrations become constant
- Macroscopic events (observable, e.g. colour change) result from countless microscopic events (molecular-level, e.g. collisions, bond breaking/forming)
- Dynamic equilibrium: both forward and reverse reactions continue indefinitely at equal rates; applies to chemical reactions and physical changes (e.g. liquid-vapour, ice-water)
- Conditions for equilibrium: reaction must be reversible; system must be closed
- Characteristics: constant concentrations; approachable from either direction; catalyst does not change position/ K_c , only speeds attainment; K_c depends only on temperature
- Pure solids/liquids excluded from K_c expression (their concentration does not change)
- Homogeneous equilibrium: all species same phase; heterogeneous equilibrium: species in more than one phase
- $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ for $aA + bB \rightleftharpoons cC + dD$; derived from $K_c = k_f/k_r$ using the law of mass action
- Four equilibrium constants: K_c (concentration), K_p (partial pressure), K_n (moles), K_x (mole fraction); $K_p = K_c(RT)^{\Delta n}$, $K_p = K_x(P)^{\Delta n}$, $K_p = K_n(N)^{\Delta n}$; all equal when $\Delta n = 0$
- Le Chatelier's principle: a system at equilibrium shifts to counteract any imposed disturbance
- Concentration change: shifts position to consume the addition/replace the removal; pressure/volume change: only matters if gas moles differ, shifts toward fewer gas moles side under higher pressure
- Temperature is the only factor that changes K_c itself: exothermic reaction, T up $\rightarrow K_c$ down; endothermic reaction, T up $\rightarrow K_c$ up
- Haber process (exothermic, moles decrease forward): industrial compromise of $\sim 400^\circ\text{C}$, 200-300 atm, iron catalyst; Contact process (exothermic): ~ 1 atm, V_2O_5 catalyst, 400-500°C after cooling



Exam Tips

- Remember K_c depends only on temperature -- changes in concentration, pressure, or volume shift the position of equilibrium but never change the numerical value of K_c itself
- Always leave pure solids and pure liquids out of an equilibrium constant expression -- only include species whose concentration can actually change (gases and species in solution)
- When converting between K_p and K_c , calculate Δn (moles of gaseous products minus moles of gaseous reactants) from the balanced equation first, and double check its sign before substituting into $K_p = K_c(RT)^{\Delta n}$
- For pressure/volume questions, first check whether the total moles of gas differ between reactants and products -- if they are equal, pressure and volume changes have no effect on the equilibrium position at all
- For temperature questions, first identify whether the given reaction is exothermic or endothermic from its ΔH sign, then apply the rule that raising temperature always favours whichever direction absorbs heat
- When explaining industrial conditions (Haber process, contact process), remember the answer is almost always a compromise between the yield favoured by Le Chatelier's principle and the reaction rate needed for the process to be economically practical



Chapter 9: Acid-Base Chemistry

Acid-base chemistry extends the everyday idea of sour-tasting acids and bitter-tasting bases into a precise, quantitative framework. The Bronsted-Lowry concept defines acids and bases as proton donors and proton acceptors, introducing the idea of conjugate acid-base pairs, while the broader Lewis concept defines them instead by the donation and acceptance of an electron pair, extending acid-base behaviour to reactions that do not involve protons at all. Water's own self-ionization defines the ionic product of water, K_w , from which the pH and pOH scales are built to conveniently express the very low ion concentrations found in aqueous solutions.

The chapter then applies this framework to weak acids, whose ionization constant, K_a , measures how far they dissociate, and shows how adding a common ion suppresses the ionization of a weak electrolyte, an effect exploited in buffer solutions that resist changes in pH. The same equilibrium ideas explain why sparingly soluble salts have a fixed solubility product, K_{sp} , that governs their solubility and can be used to predict precipitation, why aqueous solutions of certain salts are acidic or basic due to hydrolysis, and how acid-base indicators and titration curves are used together to determine the concentration of an unknown acid or base experimentally.

Learning Objectives

- Define conjugate acid-base pairs according to the Bronsted-Lowry concept and identify them in given reactions
- Distinguish Lewis acids, which accept an electron pair, from Lewis bases, which donate an electron pair to form a coordinate covalent bond
- Define K_w , pH, K_a , and pK_a mathematically and use them in calculations
- Calculate $[H^+(aq)]$ and pH values for strong acids, strong alkalis, weak acids, and weak alkalis
- Calculate the $[H_3O^+]$ of a weak acid solution given its K_a and molar concentration



- Apply the common ion effect to explain why the solubility of a substance changes in a solution containing a common ion
- Calculate the pH of a buffer solution given appropriate data, using the Henderson equation
- Construct the expression for a solubility product, K_{sp} , and use it to calculate ionic concentrations and predict precipitation
- Use the concept of hydrolysis, and of conjugate acids and bases, to explain why aqueous solutions of certain salts are acidic or basic
- Select a suitable indicator for an acid-base titration given appropriate data, and interpret acid-base titration curves

Key Concepts

9.1 Bronsted-Lowry Concept and Conjugate Acid-Base Pairs

In 1923, Bronsted and Lowry independently extended the Arrhenius theory, which was limited to acid-base reactions in water, by describing acid-base reactions as proton-transfer reactions: a Bronsted-Lowry acid is the species that donates a proton (H^+) in a reaction, and a Bronsted-Lowry base is the species that accepts it. When HCl dissolves in water, HCl (the acid) donates a proton to H_2O (the base), forming $H_3O^+(aq)$ and $Cl^-(aq)$: $HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$. The species formed when a base accepts a proton is called its conjugate acid, so H_3O^+ is the conjugate acid of H_2O , and the species formed when an acid donates a proton is called its conjugate base, so Cl^- is the conjugate base of HCl; $HCl-Cl^-$ and $H_2O-H_3O^+$ are conjugate acid-base pairs.

When ammonia dissolves in water, $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$, the roles reverse: H_2O now donates a proton and acts as the acid, while NH_3 accepts it and acts as the base, producing the conjugate pairs $NH_3-NH_4^+$ and H_2O-OH^- . Because water can act as either an acid or a base depending on the other species present, it is described as amphoteric. The Bronsted-Lowry concept also applies beyond aqueous solution: in the solventless reaction $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$, HCl still acts as the acid, donating a proton directly to NH_3 , which acts as the base, even though no hydroxide ion is present anywhere in the reaction.



9.2 Lewis Concept of Acids and Bases

In 1923, G.N. Lewis proposed a still more general definition of acid-base behaviour based on electron pairs rather than protons: a Lewis acid is any species that can accept a pair of electrons, and a Lewis base is any species that can donate a pair of electrons, with a Lewis acid-base reaction occurring when the base donates its electron pair to the acid to form a coordinate covalent bond. In the reaction of silver ions with ammonia, each of two NH_3 molecules, acting as Lewis bases, donates a lone pair to the positively charged Ag^+ ion, the Lewis acid, forming the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$.

Boron trifluoride, BF_3 , has only six electrons around boron and an incomplete octet, so it readily accepts an electron pair and behaves as a strong Lewis acid, reacting with Lewis bases such as the fluoride ion, which donates one of its lone pairs to form BF_4^- . Every Bronsted-Lowry acid and base is also a Lewis acid and base, since donating or accepting a proton always involves an electron pair, but the Lewis concept is broader, since it also classifies species such as BF_3 as acids even though no proton is transferred at all.

9.3 Ionic Product of Water (K_w)

Pure water conducts electricity only very weakly, but measurably, because it undergoes self-ionization: $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$, or more simply $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$. The equilibrium constant for this reaction, $K_c = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}]$, has a value of $1.8 \times 10^{-16} \text{ mol dm}^{-3}$; since the concentration of water itself, about 55.5 mol dm^{-3} (1000 g dm^{-3} divided by 18 g mol^{-1}), remains essentially constant because only a tiny fraction of water molecules ever ionize, this constant concentration can be combined with K_c to give a new constant, $K_w = K_c[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$, equal to 1.0×10^{-14} at 25 degrees C.

K_w , the ionic product of water, or dissociation constant of water, increases roughly 75-fold between 0 and 100 degrees C, since ionization, like most equilibria, is temperature dependent. In neutral water, $[\text{H}^+] = [\text{OH}^-]$, so $[\text{H}^+]^2 = 10^{-14}$ and $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$ at 25 degrees C. Adding an acid or a base to water changes the relative concentrations of H^+ and OH^- , making $[\text{H}^+] > [\text{OH}^-]$ in acidic solution or $[\text{OH}^-] > [\text{H}^+]$ in basic solution, but the value of



K_w itself remains constant at 1.0×10^{-14} at a given temperature regardless of what has been dissolved.

9.4 pH and pOH

Because the concentrations of H^+ and OH^- in aqueous solutions are usually far too small to be conveniently written or used in calculations, the biochemist Sorenson introduced the pH and pOH scales in 1909: $pH = -\log[H^+]$ and $pOH = -\log[OH^-]$. For neutral water, $[H^+] = [OH^-] = 10^{-7} \text{ mol dm}^{-3}$, so $pH = pOH = 7$; taking the logarithm of the K_w expression gives the general relationship $pH + pOH = 14$ at 25 degrees C, and pH normally ranges from 0 to 14 at this temperature, though solutions with pH below 0 or above 14 do exist.

Given the pH of a solution, both $[H^+]$ and $[OH^-]$ can be recovered: for a solution of pH 9.2, $pOH = 14 - 9.2 = 4.8$, so $[H^+] = 10^{-9.2}$, approximately $6.3 \times 10^{-10} \text{ mol dm}^{-3}$, and $[OH^-] = 10^{-4.8}$, approximately $1.6 \times 10^{-5} \text{ mol dm}^{-3}$, giving $K_w = (6.3 \times 10^{-10})(1.6 \times 10^{-5})$, approximately 1.0×10^{-14} , consistent with the known value of K_w at 25 degrees C. Conversely, if $[H^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$, then $[OH^-] = K_w/[H^+] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$, and $pH = pOH = 7$, confirming the solution is neutral.

9.5 Ionization Constant of Acids (K_a) and Calculating $[H_3O^+]$ for Weak Acids

Many acids are weak electrolytes that ionize far less than 100 percent when dissolved in water; the ionization constant, K_a , is the quantitative measure of how strong or weak such an acid is. For a weak acid HA, $HA + H_2O \rightleftharpoons H_3O^+ + A^-$, and following the same reasoning used for K_w , the equilibrium constant $K_c = [H_3O^+][A^-]/([HA][H_2O])$ is combined with the near-constant concentration of water to give $K_a = [H_3O^+][A^-]/[HA]$. Acids are classified by their K_a value: K_a less than 10^{-3} indicates a weak acid, K_a between 1 and 10^{-3} indicates a moderately strong acid, and K_a greater than 1 indicates a strong acid; HCl (K_a roughly 10^6) is very strong, while HF ($K_a = 6.7 \times 10^{-5}$) and acetic acid ($K_a = 1.85 \times 10^{-5}$) are weak.

For a weak acid of initial concentration C , at equilibrium $[H_3O^+] = [A^-] = x$ and $[HA] = C - x$, so $K_a = x^2/(C - x)$; since x is usually very small compared with C for a weak acid, this simplifies to K_a is approximately x^2/C , so x , the equilibrium



$[H_3O^+]$, is approximately the square root of (K_a multiplied by C). For example, a 0.1 M solution of acetic acid with $K_a = 1.8 \times 10^{-5}$ gives $[H_3O^+]$ approximately equal to the square root of $(1.8 \times 10^{-5} \times 0.1)$, approximately $1.34 \times 10^{-3} \text{ mol dm}^{-3}$.

9.6 Common Ion Effect

The common ion effect is the suppression of the ionization of a weak electrolyte caused by adding to the solution an ion that it already produces. Sodium chloride, which is fully ionized in solution, can be purified from brine by passing hydrogen chloride gas through it: the added Cl^- from HCl increases the total $[Cl^-]$ in solution, and to keep the equilibrium constant for $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$ unchanged, the system responds by crystallizing NaCl out of solution.

The same principle has several important applications: the solubility of sparingly soluble potassium chlorate, $KClO_3$, is suppressed by adding more soluble potassium chloride, KCl , since K^+ is the common ion; the dissociation of weak hydrogen sulfide, H_2S , is suppressed by adding hydrochloric acid, since H^+ is the common ion, which lowers $[S^{2-}]$ enough to selectively precipitate only the group II basic radicals during qualitative salt analysis; and adding ammonium chloride, NH_4Cl , to an ammonia solution suppresses $[OH^-]$, since NH_4^+ is the common ion, a combination used as the group reagent for group III basic radicals. The common ion effect is central to both qualitative analysis and the preparation of buffer solutions.

9.7 Buffer Solutions and the Henderson Equation

A buffer solution is one that resists changes in its pH when a small amount of acid or base is added to it, and whose pH does not significantly change on dilution or standing. Buffers are usually prepared in one of two ways: mixing a weak acid with its salt of a strong base gives an acidic buffer, pH less than 7, such as acetic acid with sodium acetate; mixing a weak base with its salt of a strong acid gives a basic buffer, pH greater than 7, such as ammonium hydroxide with ammonium chloride. In an acetic acid-sodium acetate buffer, the added CH_3COO^- from the fully-ionized salt suppresses the already limited ionization of the weak acetic acid by the common ion effect, and the buffer then acts as a large reservoir of both CH_3COOH and CH_3COO^- : added H_3O^+ reacts with the



reservoir of CH_3COO^- to reform CH_3COOH , while added OH^- reacts with H_3O^+ to form water, replenished from further ionization of CH_3COOH , so in both cases the pH changes only very slightly.

The pH of a buffer is calculated using the Henderson equation, $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Salt}]}{[\text{Acid}]}\right)$, which shows that the buffer's pH depends on two factors: the pK_a of the acid used, and the ratio of the concentrations of salt to acid. When the salt and acid concentrations are equal, the log term becomes $\log(1) = 0$, so $\text{pH} = \text{pK}_a$ exactly; for an acetic acid-sodium acetate buffer with equal concentrations of both components, this gives $\text{pH} = \text{pK}_a = 4.74$. This is why buffers are usually prepared with roughly equal concentrations of acid and salt, since it makes pK_a , a fixed property of the chosen acid, the dominant factor controlling the buffer's pH. The body's own bicarbonate buffering system keeps blood pH stable, and injectable medicines are formulated as buffers for the same reason.

9.8 Solubility Product (K_{sp}) and Its Applications

Unlike freely soluble salts such as NaCl , which dissociate essentially completely, sparingly soluble salts such as PbSO_4 reach an equilibrium between the undissolved solid and its dissolved ions: $\text{PbSO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$. Because the concentration of the undissolved solid remains constant, it is combined with K_c to give the solubility product, $K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$, equal to 1.6×10^{-8} at 25 degrees C for PbSO_4 ; in general, K_{sp} is the product of the molar concentrations of a sparingly soluble salt's ions at equilibrium, each raised to its coefficient in the balanced equation, and is usually a very small, temperature-dependent quantity.

The solubility product has three major applications. First, it allows the molar solubility, S , of a salt to be calculated: for $\text{Ca}(\text{OH})_2$, $K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = S(2S)^2 = 4S^3$, and with $K_{\text{sp}} = 6.5 \times 10^{-6}$, solving gives S approximately $1.18 \times 10^{-2} \text{ mol dm}^{-3}$. Second, the common ion effect reduces the solubility of a sparingly soluble salt: adding soluble Na_2CrO_4 to a saturated solution of PbCrO_4 increases $[\text{CrO}_4^{2-}]$, shifting the equilibrium to the left and decreasing solubility to keep K_{sp} constant. Third, comparing the ionic product of a mixture (the concentrations of the ions actually present, multiplied together in the same way as K_{sp}) with the true K_{sp} value predicts whether precipitation will occur: if the ionic product exceeds K_{sp} , the solution is supersaturated and precipitation



occurs; if it equals K_{sp} , the solution is exactly saturated; and if it is less than K_{sp} , the solution is unsaturated and no precipitation occurs. For example, mixing $10^{-2} \text{ mol dm}^{-3} \text{ Ca}^{2+}$ with $10^{-2} \text{ mol dm}^{-3} \text{ SO}_4^{2-}$ gives an ionic product of 2.5×10^{-5} , which exceeds the K_{sp} of CaSO_4 (2×10^{-5}), so CaSO_4 precipitates.

9.9 Salt Hydrolysis

When a salt dissolves in water, its ions can react with water in a process called hydrolysis, which may make the resulting solution acidic, basic, or neutral depending on the strength of the acid and base from which the salt was originally formed. A salt of a strong acid and a strong base, such as NaCl , gives a neutral solution, since neither the conjugate base of the strong acid (Cl^-) nor the conjugate acid of the strong base (Na^+) reacts significantly with water. A salt of a strong acid and a weak base, such as NH_4Cl , gives an acidic solution, since the conjugate acid of the weak base, NH_4^+ , hydrolyzes to produce H_3O^+ : $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$, while Cl^- again does not react.

A salt of a weak acid and a strong base, such as sodium acetate, CH_3COONa , gives a basic solution, since the conjugate base of the weak acid, CH_3COO^- , hydrolyzes to produce OH^- : $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$, while Na^+ does not react. A salt of a weak acid and a weak base, such as ammonium acetate, produces both a hydrolyzing cation (NH_4^+ , producing H_3O^+) and a hydrolyzing anion (CH_3COO^- , producing OH^-) at the same time, so the resulting pH, which may be acidic, basic, or nearly neutral, depends on the relative strengths of the two conjugate species involved.

9.10 Acid-Base Indicators and Titration Curves

An acid-base indicator is a substance, usually a weak organic acid or base, that changes colour to mark a titration's endpoint; a weak-acid indicator, $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$, has different colours in its unionized (HIn) and ionized (In^-) forms. In acidic solution, the equilibrium shifts toward HIn , showing the acid colour; in basic solution, OH^- removes H^+ and the equilibrium shifts toward In^- , showing the base colour. Each indicator changes colour over a characteristic pH range of about 2 units; for example, methyl red changes from red to yellow between pH 4.4 and 6.2. A suitable indicator for a given titration should have a colour-change range close to the equivalence point, the point at which the amount of titrant



added exactly matches the amount of analyte present, and should show a sharp, easily observed colour change there; the endpoint, where the indicator visibly changes colour, should be as close as possible to this true equivalence point.

A titration curve, a plot of pH against volume of titrant added, shows how the pH changes throughout a titration and helps in choosing a suitable indicator. In a strong acid-strong base titration, such as HCl with NaOH, the pH starts very low, rises gradually, then rises very steeply through pH 7.0 exactly at the equivalence point, so an indicator such as phenolphthalein, which changes colour between pH 8.2 and 10.0, works well. In a strong acid-weak base titration, such as HCl with aqueous NH_3 , the initial pH is only moderately basic, the curve passes through a buffer-like region of gradual pH change before the equivalence point, and the equivalence point itself falls below pH 7 (around pH 5.27) because the conjugate acid, NH_4^+ , formed at that point hydrolyzes and makes the solution acidic; methyl orange, which changes colour between pH 3.2 and 4.5, is a suitable indicator for this type of titration.

Important Definitions

What is a Bronsted-Lowry acid?

A species that donates a proton (H^+) in a proton-transfer reaction.

What is a Bronsted-Lowry base?

A species that accepts a proton (H^+) in a proton-transfer reaction.

What is a conjugate acid-base pair?

Two species that differ from each other by the gain or loss of a single proton.

What is a Lewis acid?

Any species that can accept a pair of electrons to form a coordinate covalent bond.

What is a Lewis base?

Any species that can donate a pair of electrons to form a coordinate covalent bond.

What is the ionic product of water (K_w)?

The equilibrium constant $[\text{H}^+][\text{OH}^-]$ for the self-ionization of water, equal to 1.0×10^{-14} at 25 degrees C.



What is pH?

The negative logarithm (base 10) of the hydrogen ion concentration, $\text{pH} = -\log[\text{H}^+]$.

What is the ionization constant of an acid (K_a)?

The equilibrium constant $[\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$ that measures how far a weak acid HA dissociates in water.

What is the common ion effect?

The suppression of the ionization of a weak electrolyte caused by adding an ion that it has in common with another dissolved substance.

What is the solubility product (K_{sp})?

The product of the molar concentrations of the ions of a sparingly soluble salt at equilibrium, each raised to its stoichiometric coefficient.

Key Facts and Relations

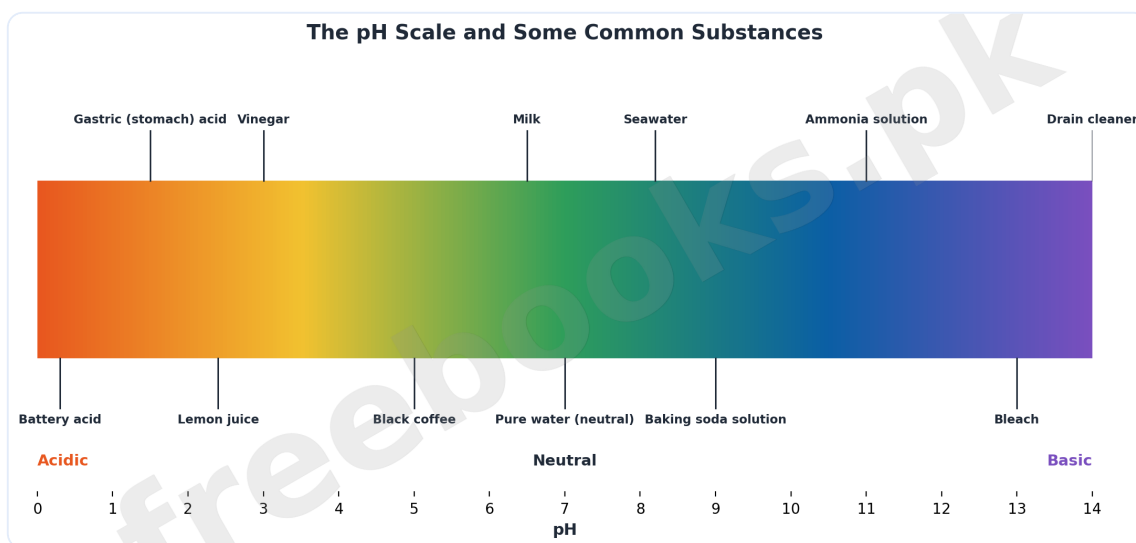
Topic	Key Fact / Relation
Ionic product of water	$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ (at 25 degrees C)
pH	$\text{pH} = -\log[\text{H}^+]$
pOH	$\text{pOH} = -\log[\text{OH}^-]$
Relationship between pH and pOH	$\text{pH} + \text{pOH} = 14$ (at 25 degrees C)
Acid dissociation constant	$K_a = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}]$
$[\text{H}_3\text{O}^+]$ for a weak acid of concentration C	$[\text{H}_3\text{O}^+]$ approximately equal to square root of ($K_a \times C$)
Henderson equation (buffer pH)	$\text{pH} = \text{p}K_a + \log([\text{Salt}]/[\text{Acid}])$
Buffer pH when $[\text{Salt}] = [\text{Acid}]$	$\text{pH} = \text{p}K_a$
Solubility product (general)	$K_{sp} = [\text{Cation}]^m [\text{Anion}]^n$



Topic	Key Fact / Relation
Precipitation criterion	Ionic product $> K_{sp}$: precipitates; $= K_{sp}$: saturated; $< K_{sp}$: unsaturated, no precipitate

Diagrams

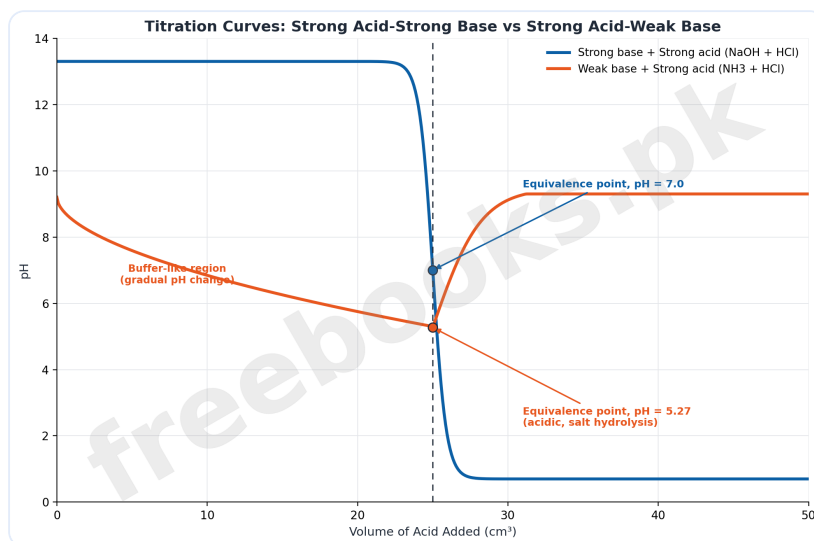
The pH Scale and Some Common Substances: A colour-graded pH scale from 0 to 14 showing where common household and biological substances fall, from strongly acidic battery acid to strongly basic drain cleaner



The pH Scale and Some Common Substances

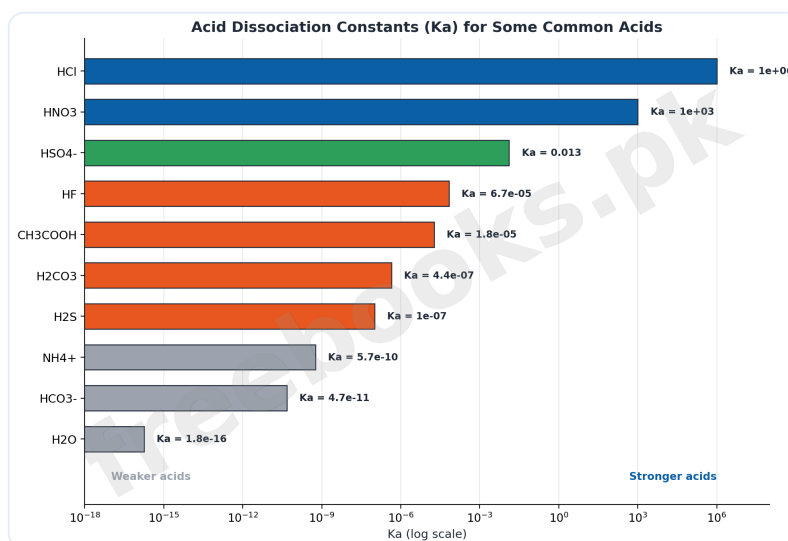
Titration Curves: Strong Acid-Strong Base vs Strong Acid-Weak Base: A comparison of pH vs volume of titrant curves for a strong acid-strong base titration and a strong acid-weak base titration, showing their different equivalence point pH values and the buffer-like region before the weak base's equivalence point





Titration Curves: Strong Acid-Strong Base vs Strong Acid-Weak Base

Acid Dissociation Constants (K_a) for Some Common Acids: A log-scale bar chart comparing the K_a values of several common acids, from very strong acids like HCl to the very weak self-ionization of water, illustrating the huge range of acid strengths



Acid Dissociation Constants (K_a) for Some Common Acids

Short Questions & Answers

Why is water described as amphoteric?

Water can act as either a Bronsted-Lowry acid or a Bronsted-Lowry base depending on what it reacts with; it donates a proton to ammonia, acting as an acid, but accepts a proton from HCl, acting as a base, so it can behave either way depending on the strength of the other reactant.



Why is BF₃ considered a Lewis acid even though it contains no hydrogen and cannot donate a proton?

The Lewis definition of an acid depends only on the ability to accept a pair of electrons to form a coordinate covalent bond, not on proton transfer; because boron in BF₃ has an incomplete octet and can accept a lone pair from a Lewis base such as F⁻, BF₃ qualifies as a Lewis acid despite having no proton-donating ability at all.

Why does the value of K_w stay the same when an acid or a base is added to water, even though [H⁺] and [OH⁻] individually change?

K_w is an equilibrium constant that depends only on temperature, not on the specific concentrations of H⁺ and OH⁻ present; adding acid or base shifts the relative amounts of H⁺ and OH⁻ away from equality, but their product, [H⁺][OH⁻], remains fixed at K_w as long as the temperature does not change.

Why was the pH scale introduced instead of simply using [H⁺] directly?

The concentrations of H⁺ in aqueous solutions typically range across many powers of ten, from around 1 mol dm⁻³ down to 10⁻¹⁴ mol dm⁻³ or smaller, making them awkward to write and compare directly; taking the negative logarithm compresses this huge range into small, easily comparable numbers, usually between 0 and 14.

Why does the approximation [H₃O⁺] is approximately equal to the square root of (K_a x C) only work for weak acids?

This approximation assumes that x, the amount of acid that ionizes, is negligible compared with C, the initial concentration, so that C - x can be replaced with C; this is a good assumption only when the acid ionizes to a very small extent, which is true for weak acids but not for strong acids, which ionize almost completely.

Why does passing HCl gas through a saturated NaCl solution cause solid NaCl to crystallize out?

The added HCl greatly increases the concentration of Cl⁻, a common ion also produced by NaCl; to keep the equilibrium constant for NaCl(s) ⇌ Na⁺(aq) + Cl⁻(aq) unchanged, the equilibrium shifts to the left, converting dissolved Na⁺ and Cl⁻ back into solid NaCl and crystallizing it out of solution.



Why does a mixture of a weak acid and its salt resist changes in pH when a small amount of strong acid is added?

The buffer contains a large reservoir of the conjugate base (from the salt) that can react with the added H_3O^+ to reform the weak acid, consuming most of the added acid before it can significantly raise the free $[\text{H}_3\text{O}^+]$ concentration; because this reservoir is large compared with the small amount of acid added, the pH changes only slightly.

Why is the pH of a buffer equal to the pKa of its acid when the salt and acid concentrations are equal?

The Henderson equation, $\text{pH} = \text{pKa} + \log([\text{Salt}]/[\text{Acid}])$, reduces to $\text{pH} = \text{pKa} + \log(1)$ when the salt and acid concentrations are equal, and $\log(1) = 0$, so the entire salt/acid ratio term vanishes, leaving the buffer's pH equal to the fixed pKa value of the acid being used.

Why does adding Na_2CrO_4 to a saturated PbCrO_4 solution decrease the solubility of PbCrO_4 rather than increase it?

Na_2CrO_4 supplies additional CrO_4^{2-} ions, a common ion also produced by dissolving PbCrO_4 ; to keep the solubility product, $K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}]$, constant despite the higher $[\text{CrO}_4^{2-}]$, the equilibrium must shift toward the solid, decreasing $[\text{Pb}^{2+}]$ and therefore decreasing how much PbCrO_4 remains dissolved.

Why does a solution of ammonium chloride (NH_4Cl) turn out to be acidic rather than neutral?

NH_4Cl is the salt of a strong acid (HCl) and a weak base (NH_3); its chloride ion, the conjugate base of a strong acid, does not react with water, but its ammonium ion, the conjugate acid of a weak base, does hydrolyze, $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$, producing excess H_3O^+ and making the solution acidic.



Long Questions & Answers

Explain the Bronsted-Lowry and Lewis concepts of acids and bases, and describe how each defines conjugate acid-base pairs and coordinate covalent bond formation.

What is the key difference between how the Bronsted-Lowry and Lewis concepts define an acid?

The Bronsted-Lowry concept defines an acid specifically as a proton (H^+) donor, while the Lewis concept defines an acid more broadly as any species that can accept a pair of electrons to form a coordinate covalent bond; every Bronsted-Lowry acid is also a Lewis acid, but the Lewis concept additionally covers species, such as BF_3 , that have no proton to donate at all.

How are conjugate acid and conjugate base defined in the Bronsted-Lowry concept?

When an acid donates a proton, the species left behind is called its conjugate base; when a base accepts that proton, the species formed is called its conjugate acid; together, the original acid and its conjugate base, or the original base and its conjugate acid, make up a conjugate acid-base pair.

Why is water considered amphoteric under the Bronsted-Lowry concept?

Water can either donate a proton, acting as an acid, as when it reacts with ammonia to form OH^- and NH_4^+ , or accept a proton, acting as a base, as when it reacts with HCl to form H_3O^+ and Cl^- ; because it can behave as either an acid or a base depending on what it reacts with, water is described as amphoteric.

How does a Lewis acid-base reaction differ chemically from a Bronsted-Lowry proton-transfer reaction?

A Bronsted-Lowry reaction transfers a proton from the acid to the base; a Lewis acid-base reaction instead transfers a pair of electrons from the base to the acid, forming a new coordinate covalent bond between them, as when ammonia donates a lone pair to a silver ion or a fluoride ion donates a lone pair to boron trifluoride.



Why is boron trifluoride, BF₃, described as a very good Lewis acid?

The boron atom in BF₃ has only six electrons in its valence shell, leaving it with an incomplete octet and a strong tendency to accept an additional electron pair to complete its octet; this makes BF₃ a highly effective electron pair acceptor, and therefore a strong Lewis acid, readily reacting with electron pair donors such as the fluoride ion.

Describe how the pH and pOH scales are derived from the ionic product of water, and explain how the ionization constant K_a is used to calculate the pH of a weak acid solution.

How is the ionic product of water, K_w, obtained from the self-ionization equilibrium of water?

The equilibrium constant for water's self-ionization, $K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$, is combined with the essentially constant concentration of water itself (about 55.5 mol dm⁻³) to give a new constant, $K_w = K_c[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$, which has the value 1.0×10^{-14} at 25 degrees C.

Why do pH and pOH always add up to 14 at 25 degrees C?

Since $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$, taking the negative logarithm of both sides gives $-\log[\text{H}^+] + (-\log[\text{OH}^-]) = -\log(10^{-14}) = 14$; because $\text{pH} = -\log[\text{H}^+]$ and $\text{pOH} = -\log[\text{OH}^-]$, this shows directly that $\text{pH} + \text{pOH} = 14$ at 25 degrees C.

How is the ionization constant, K_a, of a weak acid defined and derived?

For a weak acid HA dissociating as $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$, the equilibrium constant $K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$ is combined with the constant concentration of water in the same way K_w is derived, giving $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$, a constant that measures how far the acid dissociates at a given temperature.

How is [H₃O⁺] calculated for a weak acid of known initial concentration and K_a?

Setting up an equilibrium table shows that $[\text{H}_3\text{O}^+] = [\text{A}^-] = x$ and $[\text{HA}] = C - x$, so $K_a = \frac{x^2}{C - x}$; because x is small relative to C for a weak acid, this simplifies



to K_a approximately equal to x^2/C , which rearranges to give x , the equilibrium $[H_3O^+]$, as approximately the square root of (K_a multiplied by C).

Why does a stronger acid, such as HCl, not follow this same square-root approximation for calculating $[H_3O^+]$?

The square-root approximation depends on the ionized amount, x , being small compared with the initial concentration, C , which is only true for weak acids that dissociate to a small extent; a strong acid like HCl dissociates almost completely, so x is nearly equal to C rather than negligible compared with it, and $[H_3O^+]$ is instead found directly from the acid's initial concentration.

Multiple Choice Questions (MCQs)

In the reaction $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$, which species acts as the Bronsted-Lowry base?

- A. H_2O , because it donates a proton
- B. NH_3 , because it accepts a proton
- C. NH_4^+ , because it is positively charged
- D. OH^- , because it is negatively charged

Answer: B. NH_3 , because it accepts a proton

Explanation: NH_3 accepts a proton from H_2O to form NH_4^+ , making NH_3 the Bronsted-Lowry base and H_2O the Bronsted-Lowry acid in this reaction.

Which of the following best describes a Lewis acid?

- A. A species that donates a proton
- B. A species that donates a pair of electrons
- C. A species that accepts a pair of electrons
- D. A species that accepts a proton

Answer: C. A species that accepts a pair of electrons

Explanation: A Lewis acid is defined as any species that can accept a pair of electrons to form a coordinate covalent bond, regardless of whether a proton is involved.

If the pH of a solution is 3, what is its $[H^+]$?

- A. 3 mol dm^{-3}
- B. $1 \times 10^{-3} \text{ mol dm}^{-3}$



C. $1 \times 10^3 \text{ mol dm}^{-3}$

D. 0.3 mol dm^{-3}

Answer: B. $1 \times 10^{-3} \text{ mol dm}^{-3}$

Explanation: Since $\text{pH} = -\log[\text{H}^+]$, $[\text{H}^+] = 10^{-\text{pH}} = 10^{-3} \text{ mol dm}^{-3}$.

Which combination correctly describes the relationship between pH and pOH at 25 degrees C?

A. $\text{pH} - \text{pOH} = 14$

B. $\text{pH} \times \text{pOH} = 14$

C. $\text{pH} + \text{pOH} = 14$

D. $\text{pH} + \text{pOH} = 7$

Answer: C. $\text{pH} + \text{pOH} = 14$

Explanation: Because $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ at 25 degrees C, taking negative logarithms of both concentrations gives $\text{pH} + \text{pOH} = 14$.

A weak acid has $K_a = 4.0 \times 10^{-4}$ and an initial concentration of 0.10 mol dm^{-3} . Its approximate $[\text{H}_3\text{O}^+]$ is closest to:

A. $4.0 \times 10^{-5} \text{ mol dm}^{-3}$

B. $2.0 \times 10^{-3} \text{ mol dm}^{-3}$

C. $6.3 \times 10^{-3} \text{ mol dm}^{-3}$

D. $4.0 \times 10^{-3} \text{ mol dm}^{-3}$

Answer: C. $6.3 \times 10^{-3} \text{ mol dm}^{-3}$

Explanation: $[\text{H}_3\text{O}^+]$ is approximately the square root of $(K_a \times C) = \text{square root of } (4.0 \times 10^{-4} \times 0.10) = \text{square root of } (4.0 \times 10^{-5})$, approximately $6.3 \times 10^{-3} \text{ mol dm}^{-3}$.

Adding solid NaCl to a saturated solution of AgCl will:

A. Increase the solubility of AgCl

B. Decrease the solubility of AgCl due to the common ion effect

C. Have no effect on the solubility of AgCl

D. Convert all AgCl into a soluble complex

Answer: B. Decrease the solubility of AgCl due to the common ion effect

Explanation: Cl^- is a common ion produced by both NaCl and AgCl; increasing $[\text{Cl}^-]$ shifts the AgCl dissolution equilibrium to the left by Le Chatelier's principle (the common ion effect), decreasing the solubility of AgCl.

A buffer solution is best prepared by mixing:



- A. A strong acid and a strong base
- B. A weak acid and its salt with a strong base
- C. Two different strong acids
- D. A weak acid and a weak base of unrelated identity

Answer: B. A weak acid and its salt with a strong base

Explanation: An effective buffer is made from a weak acid together with its salt (its conjugate base) of a strong base, since this combination provides a reservoir of both HA and A⁻ that can absorb small additions of acid or base.

If the ionic product of a mixture of ions exceeds the K_{sp} of the corresponding salt, the solution is:

- A. Unsaturated, and no precipitate forms
- B. Exactly saturated, at equilibrium
- C. Supersaturated, and precipitation occurs
- D. Impossible to characterize without more data

Answer: C. Supersaturated, and precipitation occurs

Explanation: When the ionic product exceeds K_{sp}, the solution contains more dissolved ions than the equilibrium allows, so it is supersaturated and the excess salt precipitates out until the ionic product falls back to K_{sp}.

A solution of sodium acetate (CH₃COONa) in water is expected to be:

- A. Acidic, because Na⁺ hydrolyzes
- B. Basic, because CH₃COO⁻ hydrolyzes to form OH⁻
- C. Neutral, because both ions are spectators
- D. Acidic, because CH₃COO⁻ hydrolyzes to form H₃O⁺

Answer: B. Basic, because CH₃COO⁻ hydrolyzes to form OH⁻

Explanation: Sodium acetate is the salt of a weak acid (acetic acid) and a strong base (NaOH); its acetate ion, the conjugate base of a weak acid, hydrolyzes to produce OH⁻, making the solution basic, while Na⁺ does not react with water.

Which indicator is most suitable for a strong acid-weak base titration, where the equivalence point occurs below pH 7?

- A. Phenolphthalein (range 8.2-10.0)
- B. Methyl orange (range 3.2-4.5)
- C. An indicator with a range centered exactly at pH 7
- D. Any indicator, since the choice does not matter



Answer: B. Methyl orange (range 3.2-4.5)

Explanation: The equivalence point of a strong acid-weak base titration occurs below pH 7, in the acidic region, so methyl orange, which changes colour between pH 3.2 and 4.5, gives a sharp colour change close to that equivalence point.

Quick Revision Summary

- Bronsted-Lowry: acid = proton donor, base = proton acceptor; conjugate acid/base pairs differ by one proton; water is amphoteric
- Lewis concept: acid = electron pair acceptor, base = electron pair donor, forming a coordinate covalent bond; broader than Bronsted-Lowry (e.g. BF_3)
- $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 25 degrees C; constant at a given temperature regardless of acid/base added; increases with temperature
- $\text{pH} = -\log[\text{H}^+]$; $\text{pOH} = -\log[\text{OH}^-]$; $\text{pH} + \text{pOH} = 14$ at 25 degrees C; neutral water has $\text{pH} = \text{pOH} = 7$
- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$; $K_a < 10^{-3}$ weak, 10^{-3} to 1 moderately strong, > 1 strong
- For a weak acid of concentration C: $[\text{H}_3\text{O}^+]$ approximately equal to square root of $(K_a \times C)$, valid when x is small relative to C
- Common ion effect: adding a common ion suppresses ionization of a weak electrolyte (used in NaCl purification, qualitative analysis, buffers)
- Buffer solution resists pH change on adding small amounts of acid/base; acidic buffer = weak acid + its salt; basic buffer = weak base + its salt
- Henderson equation: $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Salt}]}{[\text{Acid}]}\right)$; $\text{pH} = \text{pK}_a$ when $[\text{Salt}] = [\text{Acid}]$
- K_{sp} = product of ion concentrations at equilibrium, each raised to its coefficient; used to find solubility, apply the common ion effect, and predict precipitation
- Precipitation rule: ionic product $> K_{sp}$ precipitates; $= K_{sp}$ saturated; $< K_{sp}$ unsaturated
- Salt hydrolysis: strong acid + strong base $\rightarrow$ neutral; strong acid + weak base $\rightarrow$ acidic (cation hydrolyzes); weak acid + strong base $\rightarrow$ basic (anion hydrolyzes); weak acid + weak base $\rightarrow$ depends on relative strengths



- Acid-base indicators are weak acids/bases with different colours for HIn and In⁻; choose an indicator whose colour-change range is close to the titration's equivalence point
- Strong acid-strong base titration: equivalence point pH = 7.0 (phenolphthalein suitable); strong acid-weak base titration: equivalence point pH < 7 (methyl orange suitable)

Exam Tips

- Always double check whether a question asks about the Bronsted-Lowry acid/base (proton transfer) or the Lewis acid/base (electron pair transfer) role of a species -- some species, like BF₃, only make sense under the Lewis definition
- Remember K_w only changes with temperature -- it is the same 1.0×10^{-14} in acidic, neutral, and basic solutions at 25 degrees C, even though [H⁺] and [OH⁻] individually differ
- For weak acid pH calculations, always check that x is genuinely small compared with C before using the square-root approximation; for strong acids, assume complete dissociation instead
- For buffer pH calculations, use the Henderson equation directly with [Salt] and [Acid] as given -- do not confuse which one goes in the numerator, since salt over acid, not acid over salt, gives the correct sign
- When comparing an ionic product with K_{sp} to predict precipitation, make sure the exponents on each ion concentration match the salt's actual formula (e.g. $K_{sp} = [\text{Ca}^{2+}][\text{OH}^{-}]^2$ for Ca(OH)₂, not $[\text{Ca}^{2+}][\text{OH}^{-}]$)
- For salt hydrolysis questions, first identify whether the salt's parent acid and base were strong or weak -- this alone determines whether the solution will be neutral, acidic, or basic, before doing any calculation



Chapter 10: Electrochemistry

Electrochemistry is the branch of chemistry that studies the interconversion of electrical and chemical energy through redox (reduction-oxidation) reactions, in which oxidation, the loss of electrons, and reduction, the gain of electrons, always occur together. Oxidation numbers provide a bookkeeping system for tracking electron transfer even in covalent compounds, allowing any redox reaction to be identified, its oxidizing and reducing agents pinpointed, and its equation balanced systematically using the oxidation number method.

In an electrolytic cell, an external electrical supply drives an otherwise non-spontaneous redox reaction, and the quantity of substance liberated at each electrode can be calculated precisely using the Faraday constant, which also provides a classic experimental route to the Avogadro constant. In a galvanic (voltaic) cell, by contrast, a spontaneous redox reaction generates electrical energy on its own; comparing the standard electrode potentials of two half-cells, each measured relative to the standard hydrogen electrode, predicts the direction of electron flow, the feasibility of a reaction, and the relative strength of different oxidizing and reducing agents, while the Nernst equation extends these predictions to solutions at non-standard concentrations and underlies practical applications from the activity series of metals to photovoltaic cells and water-quality testing.

Learning Objectives

- Define oxidation, reduction, and disproportionation in terms of electron transfer and changes in oxidation number, and apply oxidation number rules to identify oxidizing and reducing agents
- Balance redox equations using the oxidation number method
- Explain how an electrolytic cell converts electrical energy into chemical energy, with oxidation at the anode and reduction at the cathode
- Apply the relationship between the Faraday constant, the Avogadro constant, and the charge on the electron to calculate the mass or volume of substance liberated during electrolysis



- Describe how the Avogadro constant can be deduced experimentally by an electrolytic method
- Define standard electrode potential and standard cell potential, and describe the standard hydrogen electrode (SHE) used to measure them
- Calculate standard cell potentials by combining two standard electrode potentials, and use them to predict the feasibility of a reaction and the direction of electron flow
- Deduce the relative strength of elements, compounds, and ions as oxidizing or reducing agents from their electrode potential values
- Explain how a galvanic (voltaic) cell converts the chemical energy of a spontaneous redox reaction into electrical energy, using the Cu-Zn cell as an example
- Explain how electrode potential varies with ion concentration using the Nernst equation, and describe the activity series of metals, photovoltaic cells, and the Winkler method for measuring biochemical oxygen demand

Key Concepts

10.1 Oxidation, Reduction, and Redox Reactions

Oxidation is a process involving the loss of one or more electrons, as when Fe^{2+} loses an electron to form Fe^{3+} , or a zinc atom loses two electrons to form Zn^{2+} ; reduction is a process involving the gain of one or more electrons, as when a chlorine atom gains an electron to form Cl^- , or Cu^{2+} gains two electrons to form copper metal. Oxidation and reduction always occur together in the same reaction, since electrons lost by one species must be gained by another; reactions in which this simultaneous electron transfer occurs are called redox reactions, and familiar examples include photosynthesis, which provides food for the entire planet, and respiration, which keeps living organisms alive. Whether a substance has been oxidized or reduced during a reaction can be determined in two equivalent ways: by tracking electron transfer directly, or by tracking the resulting change in oxidation number.

10.2 Oxidation Number and Its Rules

An oxidation number, or oxidation state, is the apparent charge assigned to a single atom in a compound, molecule, or ion, and can be positive, negative, or



zero; a higher positive oxidation number means an atom is more oxidized, while a higher negative oxidation number means it is more reduced. Several rules allow oxidation numbers to be deduced systematically: the oxidation number of any uncombined element is zero; the more electronegative element in a compound or ion is assigned the negative oxidation number; many elements have fixed oxidation numbers (group 1 metals are always +1, group 2 metals always +2, halogens in binary compounds always -1, hydrogen is usually +1 except -1 in metal hydrides, and oxygen is usually -2 except -1 in peroxides and +2 in F_2O); the oxidation number of an element in a monatomic ion equals the charge on that ion; the algebraic sum of oxidation numbers in a neutral compound is zero; and the algebraic sum of oxidation numbers in a polyatomic ion equals the charge on that ion. Transition metals and many non-metals show variable oxidation states that cannot be assumed and must instead be calculated for each specific compound.

10.3 Disproportionation and Balancing Redox Equations by the Oxidation Number Method

A disproportionation reaction is a special redox reaction in which a single substance acts as both the oxidizing agent and the reducing agent, being simultaneously oxidized and reduced to give two different products with different oxidation states; the decomposition of hydrogen peroxide, $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$, is a classic example, in which oxygen (starting at -1 in H_2O_2) is simultaneously reduced to -2 in H_2O and oxidized to 0 in O_2 .

Redox equations are balanced by the oxidation number method in a fixed sequence: write the skeleton equation; identify the elements whose oxidation number changes; record these oxidation numbers above the relevant atoms and connect them with arrows showing the change; multiply species by suitable numbers so the total increase in oxidation number equals the total decrease; and finally balance every remaining atom by inspection, usually balancing all elements except nitrogen, oxygen, and hydrogen first, then nitrogen, then oxygen, then hydrogen last. If a species undergoes both an increase and a decrease in oxidation number in the same reaction, as in a disproportionation, or if some of a species reacts while some does not change oxidation state at all,



that species is written twice on the appropriate side of the equation to keep each contribution distinct.

10.4 Electrolytic Cells and Redox Reactions in Electrolysis

An electrolytic cell is a device that uses an external electrical supply to convert electrical energy into chemical energy through electrolysis; it consists of two electrodes immersed in an electrolyte, a molten ionic compound or concentrated solution of ions, connected to a source of direct current. Under this applied current, one electrode becomes the negatively charged cathode and the other the positively charged anode; positive ions (cations) migrate to the cathode, where they gain electrons and are reduced, while negative ions (anions) migrate to the anode, where they lose electrons and are oxidized, so reduction always occurs at the cathode and oxidation always occurs at the anode.

For the electrolysis of molten zinc chloride, the cathode reaction, $\text{Zn}^{2+}(\text{l}) + 2\text{e}^{-} \rightarrow \text{Zn}(\text{s})$, is a reduction, and the anode reaction, $2\text{Cl}^{-}(\text{l}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^{-}$, is an oxidation; the electrons lost at the anode exactly balance the electrons gained at the cathode, giving the overall reaction $\text{ZnCl}_2(\text{l}) \rightarrow \text{Zn}(\text{s}) + \text{Cl}_2(\text{g})$. Electrolytic cells have wide industrial use, including the electrolysis of sodium chloride to produce sodium metal and chlorine gas, the refining and electroplating of metals, and the manufacture of chemicals such as caustic soda.

10.5 Faraday's Laws: Mass Deposited During Electrolysis

The mass of a substance produced or removed at an electrode during electrolysis is proportional to the quantity of electric charge, Q , passed through the electrolyte, where $Q = I \times t$, with I the current in amperes and t the time in seconds, giving Q in coulombs. This quantity of electricity is conveniently expressed in Faradays: one Faraday (F) is the charge carried by one mole of electrons, or one mole of singly charged ions, equal to $96,500 \text{ C mol}^{-1}$; in general, the number of Faradays passed equals the number of moles of electrons gained or lost in the electrode reaction.

Because the half-equation for each electrode reaction shows exactly how many moles of electrons are needed per mole of product, the mass of product deposited can be calculated directly: depositing one mole of silver, $\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$, requires only 1 Faraday ($96,500 \text{ C}$), while depositing one mole of copper,



$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, requires 2 Faradays ($2 \times 96,500 \text{ C}$), since twice as many electrons are needed per mole of product. For example, a current of 1.50 A passed through molten lead(II) bromide for 20.0 minutes transfers a charge of $Q = 1.50 \times 20 \times 60 = 1800 \text{ C}$; since 2 Faradays (193,000 C) are needed to deposit one mole (207 g) of lead, 1800 C deposits $(207/193,000) \times 1800$, approximately 1.93 g of lead.

10.6 Avogadro's Constant by the Electrolytic Method

The Avogadro constant, N_A , the number of particles in one mole, can be determined experimentally from electrolysis, using the relationship $N_A = (\text{charge on one mole of electrons}) / (\text{charge on one electron})$, where the charge on a single electron, found by separate experiment, is approximately $1.60 \times 10^{-19} \text{ C}$. In a typical experiment, a pure copper anode and cathode are weighed, a small constant current (around 0.20 A) is passed through aqueous copper(II) sulfate for a measured time, and the electrodes are washed, dried, and reweighed; because copper may not deposit evenly on the cathode, the more reliable measurement is the decrease in mass of the anode, from which copper dissolves as Cu^{2+} ions.

In a sample calculation, a current of 0.20 A passed for 34 minutes (2040 s) transfers a charge $Q = I \times t = 408 \text{ C}$, and dissolves 0.136 g of copper from the anode; scaling up, 63.5 g of copper (one mole) would require $(408/0.136) \times 63.5$, approximately 190,500 C, and since the half-equation $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ shows that 2 moles of electrons are needed per mole of copper, the charge on one mole of electrons is $190,500/2$, approximately 95,250 C. Dividing this by the known charge on a single electron, approximately $1.60 \times 10^{-19} \text{ C}$, gives an experimental estimate for N_A that agrees closely with the accepted value of $6.02 \times 10^{23} \text{ mol}^{-1}$.

10.7 Electrode Potentials and the Standard Hydrogen Electrode

When a metal is placed in a solution of its own ions, a redox equilibrium is established between metal atoms leaving the electrode as ions (releasing electrons onto the electrode) and metal ions in solution gaining electrons and depositing back onto the electrode; the resulting difference in electric potential between the metal and the solution is called the electrode potential, and it indicates how easily that species is oxidized or reduced. For unreactive metals



such as copper, this equilibrium favours the reduced, metallic form, making Cu^{2+} ions relatively easy to reduce, while for reactive metals such as vanadium, the equilibrium favours the oxidized, ionic form, making the metal ions comparatively difficult to reduce.

The absolute electrode potential of a single half-cell cannot be measured directly, because an electrical double layer forms at the metal surface (a thin layer of excess electrons on the metal attracting a layer of cations in solution) whose potential is not independently accessible; what can be measured is the potential difference between one half-cell and a reference half-cell. The universal reference is the standard hydrogen electrode (SHE), consisting of hydrogen gas at 101 kPa in equilibrium with $1.00 \text{ mol dm}^{-3} \text{ H}^{+}$ ions over an inert platinum-black electrode, with half-equation $2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$, assigned a standard electrode potential of exactly 0.00 V, meaning hydrogen gas and hydrogen ions are defined as having an equal tendency to gain and lose electrons.

10.8 Standard Electrode Potentials and Galvanic (Voltaic) Cells

Because a half-cell's measured voltage also depends on concentration, temperature, and gas pressure, standard electrode potentials, E° , are always measured under standard conditions: 1.00 mol dm^{-3} ion concentration, 25 degrees C, 1 atmosphere gas pressure, and connection to a standard hydrogen electrode. Connecting a Cu^{2+}/Cu half-cell to the SHE gives $E^{\circ} = +0.34 \text{ V}$, showing Cu^{2+} is easier to reduce than H^{+} , while a Zn^{2+}/Zn half-cell gives $E^{\circ} = -0.76 \text{ V}$, showing Zn^{2+} is harder to reduce than H^{+} ; in general, reduction occurs at a cell's positive terminal and oxidation at its negative terminal.

A galvanic (voltaic) cell converts the chemical energy of a spontaneous, exothermic redox reaction directly into electrical energy, again with oxidation at the anode and reduction at the cathode; connecting a Zn^{2+}/Zn half-cell to a Cu^{2+}/Cu half-cell via wires (through a voltmeter) and a salt bridge, a strip of inert porous material soaked in saturated KNO_3 solution that maintains ionic balance without allowing electron flow, makes a complete Cu-Zn galvanic cell. Zinc, with the more negative E° , is oxidized at the anode, $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$, while Cu^{2+} is reduced at the cathode, $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$, giving the overall reaction $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ and a standard cell potential $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} - E^{\circ}_{\text{ox}} = (+0.34) - (-0.76) = +1.10 \text{ V}$.



10.9 Applications of E° Values: Feasibility, Electron Flow, and Oxidizing/Reducing Strength

Comparing the E° values of two half-cells immediately predicts the direction of electron flow in the external circuit: electrons flow from the half-cell with the more negative (or less positive) E° to the half-cell with the more positive (or less negative) E° , that is, from the negative pole to the positive pole of the cell. The feasibility of a proposed redox reaction can be checked by calculating $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$ for the reduction and oxidation half-reactions actually taking place: a positive E°_{cell} means the reaction is feasible, while a negative E°_{cell} means it is not. For example, $\text{Mg}^{2+} + \text{Ag}$ cannot react spontaneously to reduce Mg^{2+} ($E^\circ_{\text{cell}} = -2.32 - 0.80 = -1.52 \text{ V}$, not feasible), but the reverse combination, Ag^+ with Mg , is feasible ($E^\circ_{\text{cell}} = -0.80 - (-2.32) = +1.52 \text{ V}$).

The more positive a half-cell's E° value, the greater its tendency to proceed in the forward (reduction) direction, meaning the species on the left of its half-equation is a stronger oxidizing agent; the more negative the E° value, the greater its tendency to proceed in reverse (oxidation), meaning the species on the right is a stronger reducing agent. Since Zn^{2+}/Zn ($E^\circ = -0.76 \text{ V}$) is more negative than Mg^{2+}/Mg ($E^\circ = -2.37 \text{ V}$) is even more negative still, magnesium is a stronger reducing agent than zinc and can reduce Zn^{2+} ions to zinc metal; compounds such as KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, with high positive E° values, act as strong oxidizing agents, while compounds such as KI and FeSO_4 , with low E° values, act as reducing agents.

10.10 The Nernst Equation and the Activity Series of Metals

Electrode potential varies with ion concentration, temperature, and pressure exactly as any equilibrium does; under non-standard conditions the symbol E (without the degree sign) is used, and Le Chatelier's principle predicts that increasing the concentration of the oxidized species shifts the reduction equilibrium forward, making E more positive, while increasing the concentration of the reduced species makes E less positive. This relationship is expressed quantitatively by the Nernst equation, $E = E^\circ + (RT/zF) \ln([\text{oxidized}]/[\text{reduced}])$, which at standard temperature simplifies to $E = E^\circ + (0.059/z) \log([\text{oxidized}]/[\text{reduced}])$, where z is the number of electrons transferred; for example, a zinc electrode in 0.1 M Zn^{2+} has $E = -0.76 + (0.059/2) \log(0.1) = -0.76 - 0.03$,



approximately -0.78 V, slightly more negative than standard because the lower Zn^{2+} concentration shifts the equilibrium away from the reduced (metallic) form.

The activity series of metals ranks metals by their standard reduction potential, from the most negative (most reactive, most easily oxidized, strongest reducing agents, such as lithium and potassium, which react vigorously even with cold water) to the most positive (least reactive, hardest to oxidize, such as the noble metals silver, platinum, and gold, which resist reaction with water or dilute acid). A metal higher in the series will displace, in a single displacement reaction, any metal lower in the series from a solution of its ions, and the feasibility of any such displacement can be confirmed the same way as any redox reaction, by checking that the resulting E°_{cell} is positive; for example, $\text{Fe(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{Ag(s)}$ has $E^\circ_{\text{cell}} = -0.80 - (-0.44)$ is incorrect ordering, and using $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}} = (+0.80) - (-0.44) = +1.24 \text{ V}$, confirming the reaction is feasible.

10.11 Photovoltaic Cells and the Winkler Method (BOD and DO)

A photovoltaic cell converts light energy directly into electrical energy through the photovoltaic effect, in which photons excite electrons from a semiconductor's valence band into its conduction band; a PN junction within the cell separates these excited electrons from the positive holes left behind, generating a voltage that drives an electric current for as long as light continues to fall on the cell. As a renewable, sustainable energy source independent of fossil fuels, the photovoltaic effect underlies solar power generation, converting an essentially inexhaustible supply of sunlight into usable electricity.

Biochemical oxygen demand (BOD) is the amount of dissolved oxygen consumed by microorganisms as they biologically oxidize organic matter in a water sample over five days at a constant 25 degrees C in the dark, and is used as a measure of water pollution: dissolved oxygen (DO), normally between 5 and 8 mg/dm³ and never healthily below 5 mg/dm³, falls as BOD rises, since the same bacterial decomposition that consumes oxygen to produce a high BOD also depletes the water's available DO, giving the two quantities an inverse relationship. The Winkler method measures DO by exploiting its oxidizing properties: dissolved oxygen reacts with iodide ion to liberate iodine, and the amount of iodine formed, proportional to the original DO, is measured by titrating against sodium



thiosulfate using starch as an indicator, which turns from dark blue to colourless at the endpoint.

Important Definitions

What is oxidation?

A process involving the loss of one or more electrons by a species, resulting in an increase in its oxidation number.

What is reduction?

A process involving the gain of one or more electrons by a species, resulting in a decrease in its oxidation number.

What is a disproportionation reaction?

A redox reaction in which a single substance is simultaneously oxidized and reduced, producing two different products with different oxidation states.

What is an oxidizing agent?

A substance that oxidizes another substance by accepting electrons from it, and is itself reduced in the process.

What is an electrolytic cell?

A device that uses an external electrical supply to drive a non-spontaneous redox reaction, converting electrical energy into chemical energy.

What is the Faraday constant?

The quantity of electric charge carried by one mole of electrons (or one mole of singly charged ions), equal to $96,500 \text{ C mol}^{-1}$.

What is the standard hydrogen electrode (SHE)?

A reference half-cell consisting of hydrogen gas at 101 kPa in equilibrium with $1.00 \text{ mol dm}^{-3} \text{ H}^+$ ions over an inert platinum electrode, assigned $E^\circ = 0.00 \text{ V}$.

What is standard electrode potential (E°)?

The voltage of a half-cell measured under standard conditions relative to the standard hydrogen electrode.

What is a galvanic (voltaic) cell?



A cell in which a spontaneous, exothermic redox reaction converts chemical energy directly into electrical energy, with oxidation at the anode and reduction at the cathode.

What is the activity series of metals?

A ranking of metals by their standard reduction potentials, from most reactive (most easily oxidized) to least reactive (hardest to oxidize).

Key Facts and Relations

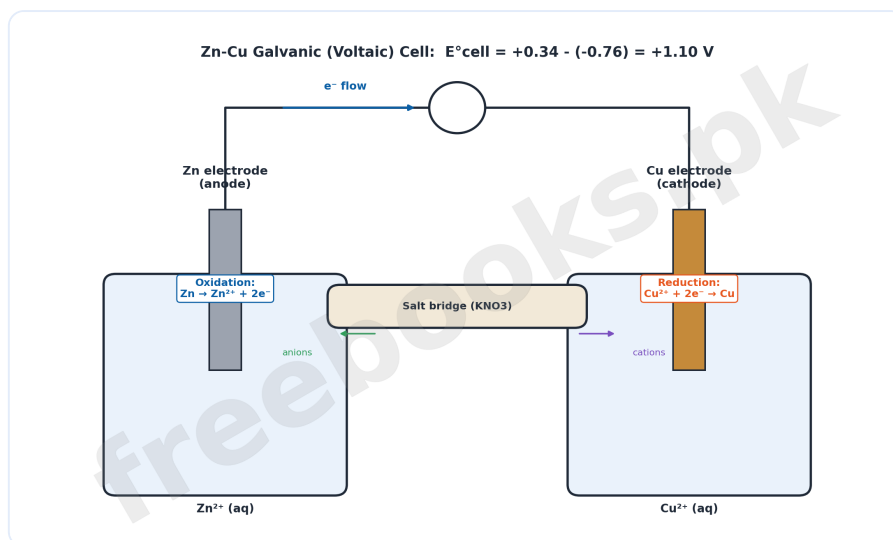
Topic	Key Fact / Relation
Charge passed during electrolysis	$Q = I \times t$ (coulombs)
Faraday constant	$1 F = 96,500 \text{ C mol}^{-1}$ (charge on 1 mole of electrons)
Number of Faradays	No. of Faradays = No. of moles of electrons gained or lost
Avogadro constant from electrolysis	$N_A = (\text{charge on 1 mole of electrons}) / (\text{charge on 1 electron})$
Standard hydrogen electrode potential	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}), E^\circ = 0.00 \text{ V}$
Standard cell potential	$E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$
Feasibility criterion	E°_{cell} positive: reaction feasible; E°_{cell} negative: reaction not feasible
Nernst equation (general)	$E = E^\circ + (RT/zF) \ln([\text{oxidized}]/[\text{reduced}])$
Nernst equation (25 degrees C)	$E = E^\circ + (0.059/z) \log([\text{oxidized}]/[\text{reduced}])$
Cu-Zn galvanic cell potential	$E^\circ_{\text{cell}} = (+0.34) - (-0.76) = +1.10 \text{ V}$

Diagrams

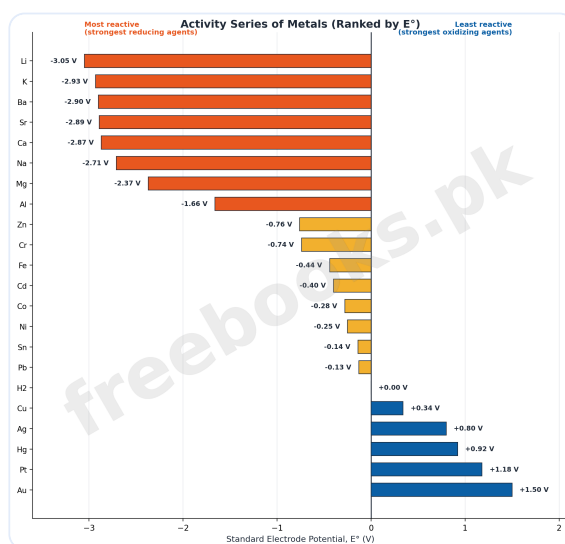
Zn-Cu Galvanic (Voltaic) Cell: A labelled schematic of a complete Cu-Zn galvanic cell, showing the zinc anode undergoing oxidation, the copper cathode



undergoing reduction, electron flow through the external wire, and ion flow through the salt bridge



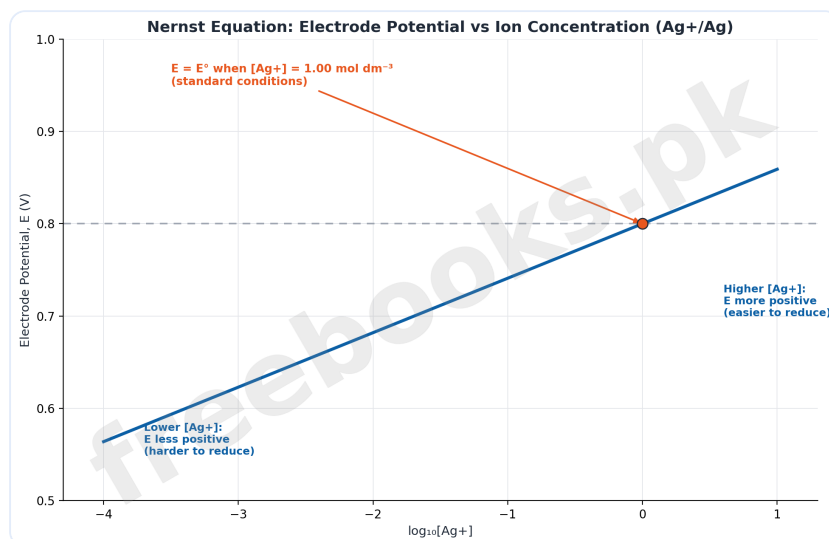
Activity Series of Metals (Ranked by E°): A ranked bar chart of standard electrode potentials for common metals, from the most reactive, strongest reducing agents at the negative end to the least reactive, strongest oxidizing agents at the positive end



Activity Series of Metals (Ranked by E°)

Nernst Equation: Electrode Potential vs Ion Concentration: A plot of electrode potential against the logarithm of ion concentration for an Ag^+/Ag half-cell, showing how E becomes more positive as ion concentration increases, consistent with the Nernst equation





Nernst Equation: Electrode Potential vs Ion Concentration

Short Questions & Answers

Why must oxidation and reduction always occur together in the same reaction?

Electrons lost by the species being oxidized cannot simply disappear; they must be gained by another species, which is thereby reduced, so oxidation and reduction are always two halves of a single electron-transfer process occurring simultaneously in what is called a redox reaction.

Why is the oxidation number of an element in its uncombined state always zero?

Oxidation number represents the apparent charge an atom would have if all bonds to different elements were fully ionic; when an element is uncombined, or bonded only to identical atoms of itself, there is no electronegativity difference to assign that apparent charge to, so the oxidation number defaults to zero.

Why is hydrogen peroxide's decomposition into water and oxygen classified as a disproportionation reaction?

In H_2O_2 , oxygen has an oxidation number of -1; in the products, oxygen ends up as -2 in water (reduced) and as 0 in O_2 gas (oxidized); because the same element, oxygen, from the same starting compound is simultaneously oxidized and reduced to give two different products, this is a disproportionation reaction.

Why does reduction always occur at the cathode, in both electrolytic and galvanic cells?



The cathode is defined as the electrode at which reduction, the gain of electrons, takes place; this definition applies consistently to both electrolytic cells, where an external current forces positive ions to migrate there and be reduced, and to galvanic cells, where the spontaneous reaction directs electrons there to reduce the oxidized species.

Why does depositing one mole of copper from Cu^{2+} require twice as many Faradays as depositing one mole of silver from Ag^+ ?

The half-equation $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ shows that two moles of electrons must be supplied to reduce one mole of Cu^{2+} ions to copper metal, whereas $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ requires only one mole of electrons per mole of silver; since one Faraday equals the charge on one mole of electrons, depositing copper requires 2 Faradays for every 1 Faraday needed for silver.

Why can the absolute electrode potential of a single half-cell, such as Cu^{2+}/Cu , not be measured directly?

Placing a metal in a solution of its ions creates an electrical double layer, a thin region of charge separation between the metal surface and the surrounding solution, whose own potential cannot be isolated and measured on its own; only the potential difference between this half-cell and a second reference half-cell, such as the standard hydrogen electrode, can actually be measured.

Why is the standard hydrogen electrode assigned an electrode potential of exactly 0.00 V?

The standard hydrogen electrode is defined, by convention, as the universal reference point against which every other standard electrode potential is measured; assigning it a value of exactly 0.00 V under standard conditions gives every other half-cell's E° value a consistent, comparable meaning relative to this single fixed reference.

Why is magnesium able to reduce Zn^{2+} ions to zinc metal, even though copper cannot?

Magnesium's standard electrode potential, $E^\circ = -2.37 \text{ V}$, is far more negative than that of zinc, $E^\circ = -0.76 \text{ V}$, making magnesium a much stronger reducing agent that readily releases electrons to Zn^{2+} ; copper's $E^\circ = +0.34 \text{ V}$ is more positive than zinc's, meaning copper is a weaker reducing agent than zinc and therefore cannot reduce Zn^{2+} ions.



Why does increasing the concentration of Zn^{2+} ions around a zinc electrode make its electrode potential more positive?

By Le Chatelier's principle, increasing $[\text{Zn}^{2+}]$ shifts the reduction equilibrium $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$ further toward the reduced, metallic form, favouring reduction; the Nernst equation captures this directly, since a higher [oxidized]/[reduced] ratio makes the logarithmic term, and therefore E , more positive.

Why is dissolved oxygen (DO) low in water with a high biochemical oxygen demand (BOD)?

A high BOD means a large amount of organic matter is present that microorganisms are actively oxidizing, a process that consumes dissolved oxygen from the water; because this biological oxidation and the water's oxygen supply are directly linked, heavy consumption of oxygen for a high BOD necessarily leaves less dissolved oxygen remaining in the water.

Long Questions & Answers

Explain how an electrolytic cell works and how the Faraday constant is used to calculate the mass of substance liberated during electrolysis, including how this method can determine the Avogadro constant.

What happens at the cathode and anode of an electrolytic cell during electrolysis?

Positive ions (cations) in the electrolyte migrate to the negatively charged cathode, where they gain electrons and are reduced, often depositing as a layer of metal or forming a gas; negative ions (anions) migrate to the positively charged anode, where they lose electrons and are oxidized, so reduction always occurs at the cathode and oxidation always occurs at the anode.

How is the quantity of charge passed during electrolysis calculated and expressed?

The charge passed, Q , is calculated from $Q = I \times t$, where I is the current in amperes and t is the time in seconds, giving Q in coulombs; this charge is often



expressed in Faradays, where one Faraday equals 96,500 C, the charge carried by exactly one mole of electrons.

How is the mass of substance deposited at an electrode calculated from the charge passed?

The half-equation for the electrode reaction shows how many moles of electrons are needed to produce one mole of product; dividing the total charge passed by the charge needed per mole of product (the number of Faradays per mole, multiplied by 96,500 C) gives the number of moles of product, which is then converted to mass using its molar mass.

How does an electrolytic experiment provide an experimental value for the Avogadro constant?

By measuring the mass of copper lost from an anode during a timed electrolysis at a known current, the charge required to deposit one mole of copper can be calculated; dividing this charge by two, since two moles of electrons are needed per mole of copper, gives the charge on one mole of electrons, which is then divided by the independently known charge on a single electron to give N_A .

Why is the decrease in mass of the anode a more reliable measurement than the increase in mass of the cathode in this experiment?

Copper deposited on the cathode does not always adhere evenly or completely to the electrode surface, introducing error into a mass-increase measurement there; the copper lost from the anode, by contrast, simply dissolves into solution as Cu^{2+} ions, giving a cleaner and more reliable measurement of the mass actually involved in the electron transfer.



Describe how standard electrode potentials are measured and used to predict the feasibility of redox reactions, and explain how the Nernst equation extends these predictions to non-standard conditions.

What are the standard conditions under which a standard electrode potential, E° , is measured?

Standard electrode potentials are measured with all ion concentrations at 1.00 mol dm^{-3} , a temperature of 25 degrees C (298 K), any gases at a pressure of 1 atmosphere (101 kPa), and the half-cell connected to a standard hydrogen electrode, which is assigned a reference value of exactly 0.00 V.

How is the standard cell potential of a galvanic cell calculated from two standard electrode potentials?

The standard cell potential is calculated as $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$, where E°_{red} is the standard electrode potential of the half-reaction undergoing reduction (at the cathode) and E°_{ox} is the standard electrode potential of the half-reaction undergoing oxidation (at the anode); a positive result confirms the combination is thermodynamically feasible as written.

How can E° values be used to predict the direction of electron flow in a galvanic cell?

Electrons in the external circuit always flow from the half-cell with the more negative (or less positive) E° value to the half-cell with the more positive (or less negative) E° value, that is, from the negative terminal of the cell to the positive terminal, since the more positive electrode has the greater tendency to accept electrons.

How does the Nernst equation adjust electrode potential for concentrations other than the standard 1.00 mol dm^{-3} ?

The Nernst equation, $E = E^\circ + (0.059/z) \log([\text{oxidized}]/[\text{reduced}])$ at 25 degrees C, adds a correction term to the standard potential based on the actual ratio of oxidized to reduced species present; when this ratio is greater than 1, E becomes



more positive than E° , and when it is less than 1, E becomes less positive (more negative) than E° .

How is the activity series of metals related to standard electrode potentials, and how is it used to predict displacement reactions?

The activity series simply ranks metals by their standard reduction potential, from most negative (most reactive, easiest to oxidize) to most positive (least reactive, hardest to oxidize); a metal higher in the series, with a more negative E° , will spontaneously displace, from solution, the ions of any metal lower in the series, which can be confirmed by checking that $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$ for the displacement reaction is positive.

Multiple Choice Questions (MCQs)

In the reaction $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$, which species is the reducing agent?

- A. Cu^{2+} , because it is reduced
- B. Zn, because it is oxidized and donates electrons
- C. Cu, because it is the product of reduction
- D. Zn^{2+} , because it is the product of oxidation

Answer: B. Zn, because it is oxidized and donates electrons

Explanation: The reducing agent is the species that gets oxidized, losing electrons to reduce another species; Zn loses electrons to become Zn^{2+} , reducing Cu^{2+} to Cu in the process, making Zn the reducing agent.

What is the oxidation number of chromium in the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$?

- A. +3
- B. +6
- C. +7
- D. +2

Answer: B. +6

Explanation: Setting $2(\text{Cr}) + 7(-2) = -2$ and solving gives $2(\text{Cr}) = 12$, so each Cr atom has an oxidation number of +6.

In electrolysis, which of the following always occurs at the anode?



- A. Reduction of cations
- B. Oxidation of anions
- C. Deposition of metal
- D. Formation of hydrogen gas

Answer: B. Oxidation of anions

Explanation: By definition, oxidation, the loss of electrons, always occurs at the anode in both electrolytic and galvanic cells; anions migrating to the anode lose electrons there.

How many Faradays of charge are required to deposit 1 mole of aluminium from Al^{3+} ions?

- A. 1 Faraday
- B. 2 Faradays
- C. 3 Faradays
- D. 4 Faradays

Answer: C. 3 Faradays

Explanation: The half-equation $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$ shows that 3 moles of electrons, and therefore 3 Faradays of charge, are needed to deposit 1 mole of aluminium metal.

The standard hydrogen electrode (SHE) is assigned a standard electrode potential of:

- A. +1.00 V
- B. -1.00 V
- C. 0.00 V
- D. It varies with temperature

Answer: C. 0.00 V

Explanation: The SHE is defined by convention as the universal reference electrode with $E^\circ = 0.00 \text{ V}$, against which every other standard electrode potential is measured.

Given $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V}$ and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$, what is E°_{cell} for a Zn-Ag galvanic cell?

- A. +0.04 V
- B. +1.56 V
- C. -1.56 V
- D. +0.76 V



Answer: B. +1.56 V

Explanation: $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}} = (+0.80) - (-0.76) = +1.56 \text{ V}$, since Ag^+ is reduced at the cathode and Zn is oxidized at the anode.

Which of the following metals is the strongest reducing agent, based on standard electrode potentials?

A. Cu ($E^\circ = +0.34 \text{ V}$)

B. Fe ($E^\circ = -0.44 \text{ V}$)

C. Mg ($E^\circ = -2.37 \text{ V}$)

D. Ag ($E^\circ = +0.80 \text{ V}$)

Answer: C. Mg ($E^\circ = -2.37 \text{ V}$)

Explanation: The more negative the standard electrode potential, the stronger the reducing agent; magnesium's $E^\circ = -2.37 \text{ V}$ is the most negative of the four, making it the strongest reducing agent listed.

According to the Nernst equation, increasing the concentration of the oxidized species in a half-cell will:

A. Decrease E, making it more negative

B. Increase E, making it more positive

C. Have no effect on E

D. Change E° but not E

Answer: B. Increase E, making it more positive

Explanation: The Nernst equation shows $E = E^\circ + (0.059/z) \log([\text{oxidized}]/[\text{reduced}])$; increasing [oxidized] increases the log term, making E more positive.

A reaction has $E^\circ_{\text{cell}} = -0.62 \text{ V}$ as written. What can be concluded?

A. The reaction is feasible as written

B. The reaction is not feasible as written, but the reverse reaction is feasible

C. The reaction proceeds very quickly

D. No conclusion can be drawn without more data

Answer: B. The reaction is not feasible as written, but the reverse reaction is feasible

Explanation: A negative E°_{cell} means the reaction as written is not thermodynamically feasible; since reversing a reaction reverses the sign of E°_{cell} , the reverse reaction would have $E^\circ_{\text{cell}} = +0.62 \text{ V}$ and would be feasible.

The Winkler method for measuring dissolved oxygen (DO) is based on which type of titration?



- A. Acid-base titration
- B. Complexometric titration
- C. Iodometric titration
- D. Precipitation titration

Answer: C. Iodometric titration

Explanation: The Winkler method relies on dissolved oxygen oxidizing iodide ions to liberate iodine, which is then titrated against sodium thiosulfate using starch indicator, an iodometric titration technique.

Quick Revision Summary

- Oxidation = loss of electrons (oxidation number increases); reduction = gain of electrons (oxidation number decreases); redox reactions involve both together
- Oxidation number rules: uncombined element = 0; more electronegative element gets negative sign; group 1 = +1, group 2 = +2, halogens (binary) = -1, H usually +1, O usually -2; monatomic ion = its charge; neutral compound sums to 0, polyatomic ion sums to its charge
- Disproportionation: one substance is simultaneously oxidized and reduced (e.g. $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$)
- Redox equations balanced by oxidation number method: identify oxidation number changes, equalize electrons gained/lost, balance rest by inspection
- Electrolytic cell: external current drives non-spontaneous reaction; reduction at cathode, oxidation at anode
- $Q = I \times t$; 1 Faraday = 96,500 C mol⁻¹ = charge on 1 mole of electrons; No. of Faradays = moles of electrons transferred
- Avogadro constant: $N_A = (\text{charge on 1 mole of electrons}) / (\text{charge on 1 electron})$, found via anode mass loss in electrolysis
- Standard hydrogen electrode (SHE): 1.00 mol dm⁻³ H⁺, 101 kPa H₂, Pt electrode, $E^\circ = 0.00 \text{ V}$, universal reference
- Standard electrode potential (E°): measured at 1.00 mol dm⁻³, 25 degrees C, 1 atm, relative to SHE
- Galvanic (voltaic) cell: spontaneous redox reaction generates electricity; oxidation at anode, reduction at cathode; connected via wire + salt bridge



- $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$; positive E°_{cell} = feasible reaction; electrons flow from more negative to more positive E° half-cell
- More positive E° = stronger oxidizing agent (species on left of half-equation); more negative E° = stronger reducing agent (species on right)
- Nernst equation: $E = E^\circ + (0.059/z) \log([\text{oxidized}]/[\text{reduced}])$ at 25 degrees C; higher [oxidized] makes E more positive
- Activity series: metals ranked by E° , most negative (most reactive) to most positive (least reactive); higher metal displaces lower metal's ions
- Photovoltaic cells convert light to electricity via the photovoltaic effect in a PN junction; Winkler method (iodometric titration) measures DO, which is inversely related to BOD

Exam Tips

- When assigning oxidation numbers, apply the fixed-value rules first (group 1, group 2, halogens, H, O), then solve algebraically for the one remaining unknown element using the sum-to-zero (compound) or sum-to-charge (ion) rule
- When balancing redox equations by the oxidation number method, always check that the total increase in oxidation number equals the total decrease before balancing the remaining atoms by inspection
- Remember reduction always happens at the cathode and oxidation always happens at the anode, in both electrolytic cells and galvanic cells -- this rule never flips, even though which electrode is positive or negative does differ between the two cell types
- For electrolysis mass calculations, always start by writing the electrode half-equation to find how many moles of electrons (and therefore Faradays) are needed per mole of product, before using $Q = I \times t$
- For E°_{cell} calculations, always use $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}}$ (reduction half-cell minus oxidation half-cell), never simply add the two values without regard to which one is being reduced and which is being oxidized
- In Nernst equation problems, always identify which species is the oxidized form and which is the reduced form from the half-equation before substituting into the log term -- reversing them flips the sign of the correction to E°



Chapter 11: Hydrocarbons

Hydrocarbons are organic compounds composed of only carbon and hydrogen, and are broadly divided into aliphatic hydrocarbons, which include the open-chain and cyclic families of alkanes and cycloalkanes as well as the unsaturated alkenes and alkynes, and aromatic hydrocarbons, a special class of cyclic compounds based on benzene. Alkanes are saturated hydrocarbons named systematically through a fixed set of IUPAC rules, adopt a tetrahedral shape around each sp^3 carbon, and are largely unreactive toward polar reagents because of their strong, non-polar sigma bonds, reacting mainly through free radical substitution mechanisms such as halogenation, which proceeds through initiation, propagation, and termination steps.

Alkenes, by contrast, are unsaturated hydrocarbons containing a reactive carbon-carbon double bond formed from sp^2 hybridized carbons, and undergo electrophilic addition reactions readily because their loosely held pi electrons are exposed to attack by electrophiles; reactions such as halogenation, hydrohalogenation, hydrogenation, hydration, halohydrate formation, epoxidation, ozonolysis, and polymerization all proceed through a carbocation intermediate whose stability, and therefore the reaction's regiochemistry as summarized by Markovnikov's rule, depends on the electron-donating inductive effect of attached alkyl groups. This chapter also introduces conjugated dienes, the concept of isomerism in its structural and stereochemical forms, and organic oxidation-reduction reactions, rounding out the essential framework for understanding hydrocarbon reactivity.

Learning Objectives

- Classify hydrocarbons as aliphatic and aromatic, and describe the nomenclature of alkanes and cycloalkanes
- Explain the tetrahedral shape of alkanes and cycloalkanes, exemplified by ethane and cyclopropane, and explain the unreactive nature of alkanes toward polar reagents



- Define homolytic and heterolytic fission, and describe free radical initiation, propagation, and termination in the substitution of alkanes by halogens
- Identify organic redox reactions and explain the nomenclature of alkenes using the IUPAC system
- Explain the shape of the ethene molecule in terms of sigma and pi carbon-carbon bonds, and describe the structure and reactivity of alkenes
- Explain the terms isomerism, structural isomerism, and stereoisomerism with suitable examples
- Explain the dehydration of alcohols and dehydrohalogenation of alkyl halides for the preparation of ethene
- Describe the chemistry of alkenes through hydrogenation, hydrohalogenation, hydration, halogenation, halohydrate, epoxidation, ozonolysis, and polymerization reactions of ethene
- Explain the concept of conjugation in alkenes with alternating double bonds, and describe the mechanism of electrophilic addition using bromine/ethene and hydrogen bromide/propene as examples
- Explain the inductive effect of alkyl groups on the stability of primary, secondary, and tertiary carbocations, and use this to explain Markovnikov addition

Key Concepts

11.1 Aliphatic and Aromatic Hydrocarbons

Hydrocarbons are broadly divided into two classes: aliphatic and aromatic. Compounds that are not aromatic are called aliphatic hydrocarbons; they may be open-chain or cyclic, and saturated or unsaturated. Alkanes are acyclic aliphatic hydrocarbons, cycloalkanes are cyclic aliphatic hydrocarbons, and alkenes and alkynes are acyclic, unsaturated aliphatic hydrocarbons.

Aromatic hydrocarbons are a special class of cyclic hydrocarbons with a high carbon-to-hydrogen ratio, based on benzene (C_6H_6) or resembling compounds; benzene is the parent aromatic compound, with toluene and phenol among its derivatives. The term 'aromatic' derives from the Greek word for fragrance, reflecting the characteristic odour of many early-studied members of this class.



11.2 Nomenclature of Alkanes and Cycloalkanes

Alkanes (paraffins) are saturated hydrocarbons with general formula C_nH_{2n+2} , with methane (CH_4) the simplest member; successive members (ethane, propane, butane, pentane, and so on) each add one CH_2 unit. Removing one hydrogen atom from an alkane gives an alkyl group, named by replacing the '-ane' ending with '-yl' (e.g., methane becomes methyl, ethane becomes ethyl); alkanes with three or more carbons can yield more than one possible alkyl group (e.g., n-propyl and isopropyl from propane).

Branched alkanes are named systematically by locating the longest continuous carbon chain as the parent name; numbering the chain from the end nearer a substituent; using these numbers to specify substituent positions, with the substituent name placed before the parent name; listing multiple substituents alphabetically (ignoring multiplying prefixes like di- and tri-); repeating a locant number when two substituents share one carbon; and using di-, tri-, tetra- prefixes for identical repeated substituents. When two chains of equal length compete as the parent chain, the one with more substituents is chosen; when branching starts at equal distance from both ends, the numbering giving the lower locant at the first point of difference is used. Cycloalkanes are named by attaching the prefix 'cyclo' to the alkane name with the same number of ring carbons.

11.3 Shapes and Physical Properties of Alkanes and Cycloalkanes

Each carbon in an alkane is sp^3 hybridized, forming four single sigma bonds equidistant from each other, giving alkane molecules a tetrahedral shape with bond angles of 109.5 degrees and a C-C bond length of 1.54 angstroms. Cycloalkanes are cyclic and saturated, with all ring carbons singly bonded; cyclopropane, cyclobutane, and cyclopentane are common examples.

Alkanes with up to four carbons are gases, C_5 to C_{17} are liquids, and C_{18} and above are waxy solids; alkanes are colourless, odourless, non-polar or very weakly polar, insoluble in water but soluble in non-polar solvents such as hexane and benzene. Boiling points, melting points, and density increase with increasing carbon number, while solubility decreases with increasing molecular mass; branched-chain alkanes have lower boiling points than their straight-chain



isomers, since straight chains pack more closely and experience stronger intermolecular forces.

11.4 Bond Fission, Unreactive Nature of Alkanes, and Free Radical Substitution

Covalent bonds can break in two ways: homolytic fission, in which the bond breaks evenly to produce two free radicals (species with an unpaired electron, very reactive because of the drive to pair that electron), and heterolytic fission, in which the shared electron pair is retained entirely by one atom, producing oppositely charged ions. Alkanes are largely inert toward acids, alkalis, and oxidizing or reducing agents under ordinary conditions, because the electronegativities of carbon (2.5) and hydrogen (2.1) are similar, making C-H and C-C bonds nearly non-polar, and because sigma bonds hold their electrons tightly, making them strong and hard to break.

Under suitable conditions, alkanes undergo thermal/catalytic reactions such as combustion and cracking, and free radical substitution reactions, in which one atom or group is replaced by another via a free-radical mechanism; halogenation (reaction with Cl_2 or Br_2 in sunlight or UV light) is the classic example, and proceeds in three steps: initiation, in which UV light homolytically breaks the halogen-halogen bond to form two halogen radicals; propagation, in which a halogen radical abstracts a hydrogen from the alkane to form an alkyl radical and HX , and the alkyl radical then reacts with another halogen molecule to form the haloalkane product and regenerate a halogen radical, sustaining a chain reaction; and termination, in which two radicals combine (most often an alkyl radical with a halogen radical, or occasionally two alkyl radicals, giving a rare double-carbon alkane byproduct that provides direct evidence of the radical mechanism). Halogen reactivity follows the order $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$, with fluorine reacting violently and iodine not substituting directly because the reaction is too slow and reversible.

11.5 Nomenclature and Preparation of Alkenes

Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond, with general formula C_nH_{2n} , having two fewer hydrogens than the corresponding alkane. IUPAC naming follows rules similar to alkanes: select the



longest chain containing the C=C bond as the parent, changing the '-ane' ending to '-ene'; number the chain from the end nearer the double bond so both double-bond carbons get the lowest possible locants; designate the double bond's position using the locant of its first carbon as a prefix; and indicate substituent positions by the carbons to which they are attached.

Alkenes are prepared by elimination reactions, which remove a small molecule (such as H₂O or HX) from adjacent carbons of a saturated compound to create a double bond. Ethene can be prepared by dehydration of ethanol, heating it with excess concentrated sulfuric acid at 180 degrees C (via an ethyl hydrogen sulfate intermediate that decomposes on heating), or by dehydrohalogenation of ethyl bromide, heating it with alcoholic KOH to remove H and Br from adjacent carbons.

11.6 Physical Properties, Structure, and Reactivity of Alkenes

The first three alkenes (ethene, propene, butene) are gases at room temperature, C₅ to C₁₅ are liquids, and higher members are solids; alkenes are insoluble in water but soluble in alcohol, have a characteristic smell, burn with a luminous flame, and show weak polarity due to sp² hybridization (unlike the essentially non-polar alkanes).

In ethene, each carbon is sp² hybridized, forming three coplanar sp² orbitals (two used for C-H sigma bonds, one for a C-C sigma bond by linear overlap) plus one unhybridized p-orbital perpendicular to this plane on each carbon; lateral overlap of these two parallel p-orbitals forms a pi bond, giving the C=C double bond a sigma-plus-pi character, a trigonal planar geometry with roughly 120-degree bond angles, and a fully planar molecule. Because pi electrons lie away from the internuclear axis and are less firmly held than sigma electrons, the pi bond is comparatively weak and breaks easily, exposing alkenes to attack by electrophiles and making electrophilic addition their characteristic reaction.

11.7 Carbocations and the Inductive Effect

A carbocation is an alkyl species bearing a single positive charge on one carbon atom; carbocations are classified by how many carbon (alkyl) substituents are directly bonded to that positive carbon: none (methyl carbocation), one (primary, 1 degree), two (secondary, 2 degree), or three (tertiary, 3 degree). The inductive



effect, the polarization of a sigma bond due to the electron-withdrawing or electron-donating character of neighbouring groups, governs carbocation stability: alkyl groups have a positive inductive effect (+I), donating electron density toward the positively charged carbon and thereby reducing its charge and increasing its stability, so stability increases with the number of attached alkyl groups, making tertiary carbocations the most stable and methyl carbocations the least stable (3 degree > 2 degree > 1 degree > methyl).

Electron-withdrawing groups, such as halogen atoms, show a negative inductive effect (-I): a halogen pulls bonded electrons away from the adjacent C-C bond, creating a permanent dipole in which the halogen carries a partial negative charge and the adjacent carbon becomes partially positive. This inductive withdrawal makes a nearby carbocation less stable, the opposite effect of an electron-donating alkyl group.

11.8 Electrophilic Addition Reactions of Alkenes

Alkenes react mainly through electrophilic addition, in which an electrophile adds across the C=C double bond. The C=C bond is a region of high electron density, making it attractive to electrophiles; in the generalized mechanism, an electrophile X^+ first adds to the double bond to generate a carbocation intermediate, which is then attacked by a nucleophile Y^- to give the final addition product.

In halogenation, bromine's own electron cloud is polarized as it approaches the electron-rich double bond, making the near bromine atom act as an electrophile that accepts a pair of pi electrons to form a carbocation intermediate, which the resulting bromide ion (nucleophile) then attacks to complete the addition, decolourizing bromine water and providing a simple test for unsaturation. In hydrohalogenation, a hydrogen halide's pi-bond-attacking hydrogen adds to one alkene carbon to form a carbocation, which the halide ion then attacks; for a symmetrical alkene like ethene only one product is possible, but for an unsymmetrical alkene like propene, Markovnikov's rule (the negative part of the reagent attaches to the carbon bearing fewer hydrogens) predicts that the more stable secondary carbocation forms preferentially, explaining why 2-bromopropane is the major product and 1-bromopropane the minor one.



11.9 Further Reactions of Alkenes: Hydrogenation to Polymerization

Hydrogenation adds molecular hydrogen across the double bond in the presence of a nickel or platinum catalyst at 250-300 degrees C to give a saturated alkane, an industrially important reaction used to convert vegetable oil into margarine. Hydration adds steam across the double bond in the presence of concentrated sulfuric acid catalyst to form an alcohol, proceeding through the same carbocation-intermediate mechanism as hydrohalogenation, while halohydrin adds a halogen together with water to give a halohydrin.

Epoxidation converts an alkene into a three-membered cyclic ether (epoxide) using an oxidizing agent, and epoxides can be hydrolyzed under acidic conditions to diols. Ozonolysis oxidatively cleaves an alkene's double bond using ozone, forming an ozonide intermediate that is reduced to carbonyl compounds (aldehydes or ketones), a reaction useful for locating the position of a double bond in an unknown alkene. Polymerization (addition polymerization) joins many alkene monomers, each contributing one broken pi bond, into a long-chain polymer whose repeating unit matches the monomer with its C=C converted to a C-C single bond; ethene is polymerized industrially to make polyethylene, one of the world's most common plastics.

11.10 Conjugated Dienes

A diene is a molecule containing two C=C double bonds. In a conjugated diene, these double bonds are separated by exactly one single bond, allowing the p-orbitals on three or more consecutive carbon atoms to overlap; this extended overlap delocalizes the pi electrons across the whole conjugated system, which stabilizes the molecule and influences its reactivity compared to isolated (non-conjugated) dienes. Conjugated dienes such as 1,3-butadiene are industrially important as monomers for synthetic rubber, since their conjugated structure supports the polymerization needed to build long, rubber-like polymer chains.

11.11 Isomerism and Organic Redox Reactions

Isomers are two or more compounds sharing the same molecular formula but differing in structural formula and properties, a phenomenon called isomerism; the simplest hydrocarbon showing structural isomers is butane (C₄H₁₀), and the



number of possible isomers rises rapidly as carbon number increases. Structural isomerism, arising from different atom connectivity, appears in five forms: chain isomerism (different carbon-chain branching, e.g., n-butane vs isobutane), position isomerism (same functional group at different chain positions, e.g., 1-chloropropane vs 2-chloropropane), functional group isomerism (same molecular formula, different functional groups, e.g., ethanol vs methoxymethane), metamerism (unequal carbon distribution on either side of a functional group within the same homologous series, e.g., diethyl ether vs methoxypropane), and tautomerism (a proton shifts between atoms within the same molecule, as seen in the zwitterion form of amino acids). Stereoisomerism, in which compounds share the same structural formula but differ in the spatial arrangement of identical groups, appears as geometrical (cis-trans) isomerism and optical isomerism.

Organic redox reactions involve the oxidation or reduction of organic compounds, generally recognized by the addition or removal of oxygen or hydrogen: oxidation typically adds oxygen or removes hydrogen (as in combustion, ozonolysis, epoxidation, or the oxidation of a primary alcohol to a carboxylic acid by acidified potassium dichromate), while reduction typically adds hydrogen or removes oxygen (as in the hydrogenation of a C=C double bond to an alkane, using reducing agents such as LiAlH_4 , NaBH_4 , or tin with concentrated HCl).

Important Definitions

What are aliphatic hydrocarbons?

Hydrocarbons that are not aromatic; they may be open-chain or cyclic, and saturated or unsaturated, and include alkanes, cycloalkanes, alkenes, and alkynes.

What is an alkyl group?

The group obtained by removing one hydrogen atom from an alkane, named by replacing the '-ane' ending of the alkane with '-yl'.

What is homolytic fission?

The breaking of a covalent bond evenly, so that each atom retains one electron of the shared pair, producing two free radicals.

What is heterolytic fission?



The breaking of a covalent bond unevenly, so that one atom retains both electrons of the shared pair, producing oppositely charged ions.

What is a free radical?

A species containing an unpaired electron, which is very reactive because of the unpaired electron's tendency to become paired.

What is Markovnikov's rule?

When a polar reagent adds to an unsymmetrical alkene, the negative part of the reagent attaches to the double-bonded carbon bearing the lesser number of hydrogens.

What is a carbocation?

An alkyl group bearing a single positive charge on one of its carbon atoms, classified as methyl, primary, secondary, or tertiary based on the number of attached alkyl groups.

What is the inductive effect?

The polarization of a sigma bond caused by the electron-withdrawing or electron-donating effect of adjacent groups or atoms.

What is isomerism?

The phenomenon in which two or more compounds share the same molecular formula but have different structural formulas and properties.

What is a conjugated diene?

A molecule containing two C=C double bonds separated by a single bond, allowing delocalization of pi electrons across the system.

Key Facts and Relations

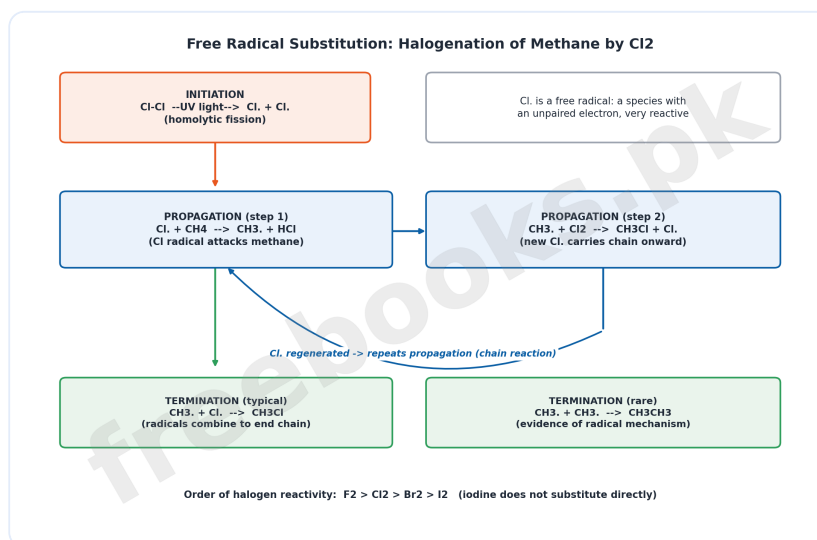
Topic	Key Fact / Relation
General formula of alkanes	C_nH_{2n+2}
General formula of alkenes	C_nH_{2n}
Halogen reactivity order (alkane substitution)	$F_2 > Cl_2 > Br_2 > I_2$
Carbocation stability order	3 degree > 2 degree > 1 degree > methyl



Topic	Key Fact / Relation
Alkane C-C bond angle / length	109.5 degrees, 1.54 Angstrom (tetrahedral, sp ³)
Alkene C=C bond angle	~120 degrees (trigonal planar, sp ²)
Dehydration of ethanol	CH ₃ CH ₂ OH --H ₂ SO ₄ , 180C--> CH ₂ =CH ₂ + H ₂ O
Dehydrohalogenation of ethyl bromide	CH ₃ CH ₂ Br + KOH(alcoholic) --heat--> CH ₂ =CH ₂ + KBr + H ₂ O
Hydrogenation of ethene	CH ₂ =CH ₂ + H ₂ --Ni, 250-300C--> CH ₃ CH ₃
Markovnikov addition (HBr + propene)	Major product: 2-bromopropane (via more stable 2 degree carbocation)

Diagrams

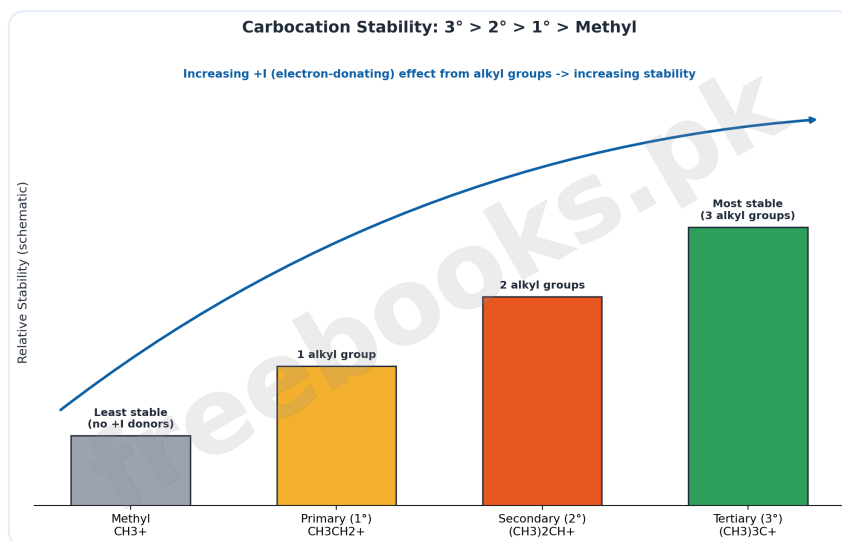
Free Radical Substitution: Halogenation of Methane: A step-by-step flow diagram of the initiation, propagation, and termination steps in the free radical chlorination of methane, showing the chain-reaction cycle and the order of halogen reactivity



Free Radical Substitution: Halogenation of Methane

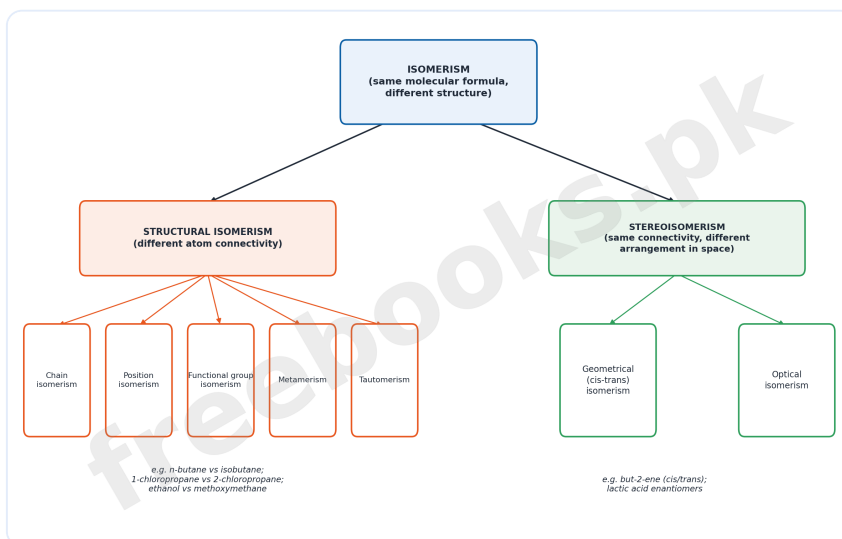
Carbocation Stability Comparison: A bar chart comparing the relative stability of methyl, primary, secondary, and tertiary carbocations, showing how the +I inductive effect of increasing numbers of alkyl groups increases stability





Carbocation Stability Comparison

Classification of Isomerism: A tree diagram classifying isomerism into structural isomerism (chain, position, functional group, metamerism, tautomerism) and stereoisomerism (geometrical and optical), with worked examples of each



Classification of Isomerism

Short Questions & Answers

Why are alkanes largely unreactive toward acids, alkalis, and oxidizing or reducing agents under ordinary conditions?

The electronegativities of carbon (2.5) and hydrogen (2.1) are close enough that the C-H and C-C bonding electrons are shared almost equally, making these bonds nearly non-polar; in addition, sigma bonds hold their electrons tightly



between the nuclei, making them strong and requiring a large amount of energy to break, so alkanes resist attack by most reagents under normal conditions.

Why does iodine not directly substitute into alkanes the way chlorine and bromine do?

The reaction of alkanes with iodine is both too slow and reversible under ordinary conditions to give a useful substitution product; this places iodine at the bottom of the reactivity order for halogenation, $F_2 > Cl_2 > Br_2 > I_2$, well below chlorine and bromine, which react readily in the presence of sunlight or UV light.

Why do branched-chain alkanes have lower boiling points than their straight-chain isomers?

Straight-chain alkane molecules can pack together more closely and have a greater surface area of contact with neighbouring molecules, allowing stronger van der Waals forces to develop between them; branched isomers are more compact and spherical, reducing this contact area and weakening the intermolecular forces, so less thermal energy is needed to separate the molecules and boil the branched compound.

Why are alkenes more reactive than alkanes, even though both contain only carbon and hydrogen?

Alkenes contain a carbon-carbon pi bond in addition to a sigma bond; because pi electrons lie away from the direct line joining the two nuclei, they are less firmly held than sigma electrons, making the pi bond comparatively weak and easy to break during a reaction, and exposing the electron-rich double bond to attack by electrophiles, which alkanes' strong, non-polar sigma bonds do not permit.

Why does tertiary carbocation have greater stability than a primary carbocation?

A tertiary carbocation is bonded to three alkyl groups, each of which has a positive inductive effect (+I) that donates electron density toward the positively charged carbon; with three such electron-donating groups pushing electron density toward it, a tertiary carbocation carries a smaller effective positive charge and is therefore energetically more stable than a primary carbocation, which has only one alkyl group donating electron density.

Why does the addition of HBr to propene give 2-bromopropane as the major product rather than 1-bromopropane?



When the pi electrons of propene attack the partially positive hydrogen of HBr, hydrogen adds to the terminal carbon (with more hydrogens already attached), generating a secondary carbocation on the middle carbon rather than a less stable primary carbocation; because the secondary carbocation intermediate is more stable and therefore forms preferentially, the bromide ion subsequently attacks it to give 2-bromopropane as the major product, consistent with Markovnikov's rule.

Why is the decolourization of bromine water used as a test for carbon-carbon double bonds?

Bromine water has a characteristic red-brown colour due to dissolved Br₂; when it is added to a compound containing a C=C double bond, the electrophilic addition reaction consumes the bromine as it adds across the double bond to form a colourless dibromo product, so the rapid loss of the red-brown colour signals the presence of unsaturation in the tested compound.

Why can ozonolysis be used to determine the position of a double bond in an unknown alkene?

Ozonolysis cleaves the C=C double bond exactly at its location, converting each half of the original alkene into a separate carbonyl compound (an aldehyde or ketone); by identifying the specific carbonyl products formed and working out which carbon atoms they correspond to in the original structure, chemists can deduce precisely where the double bond was located in the unknown alkene.

Why do conjugated dienes such as 1,3-butadiene show greater stability than non-conjugated (isolated) dienes?

In a conjugated diene, the p-orbitals on three or more consecutive carbon atoms can overlap because the two double bonds are separated by only one single bond, allowing the pi electrons to become delocalized across the whole conjugated system rather than being confined to two separate, isolated double bonds; this delocalization spreads the electron density over a larger region and lowers the overall energy of the molecule, making it more stable.

Why is the oxidation of ethanol to ethanoic acid by acidified potassium dichromate classified as an organic oxidation reaction?

Organic oxidation is generally recognized by the addition of oxygen or the removal of hydrogen from a compound; converting ethanol (C₂H₅OH) to ethanoic acid (CH₃COOH) using acidified K₂Cr₂O₇ as the oxidizing agent adds oxygen



atoms to the carbon skeleton while removing hydrogen atoms, fitting the definition of organic oxidation and explaining why $\text{K}_2\text{Cr}_2\text{O}_7$ is described as an oxidizing agent in this reaction.

Long Questions & Answers

Describe the mechanism of free radical substitution in alkanes, using the chlorination of methane as an example, and explain how the initiation, propagation, and termination steps fit together as a chain reaction.

What happens during the initiation step of methane's chlorination?

Ultraviolet light supplies enough energy to break the Cl-Cl bond homolytically, meaning each chlorine atom retains one electron of the originally shared pair; this produces two highly reactive chlorine free radicals ($\text{Cl}\cdot$), each with an unpaired electron, ready to attack the methane molecule.

What happens in the first propagation step, and what does it produce?

A chlorine radical collides with a methane molecule and abstracts one hydrogen atom, forming HCl and a methyl free radical ($\text{CH}_3\cdot$); this step converts the highly reactive $\text{Cl}\cdot$ into an equally reactive carbon-centred radical, keeping the chain of reactive species going without consuming any additional energy input.

What happens in the second propagation step, and why is it essential to the chain reaction?

The methyl radical ($\text{CH}_3\cdot$) reacts with a fresh Cl_2 molecule, forming the substitution product chloromethane (CH_3Cl) and regenerating a new chlorine radical ($\text{Cl}\cdot$); because this new $\text{Cl}\cdot$ can immediately re-enter the first propagation step and attack another methane molecule, this step is what allows the reaction to repeat itself many times over as a continuing chain reaction.



What are the possible termination steps, and why is termination necessary?

Termination occurs when two free radicals combine to form a stable, non-radical product, ending that particular chain: most commonly a methyl radical combines with a chlorine radical to give chloromethane directly, but occasionally two methyl radicals combine to give ethane (CH_3CH_3); termination is necessary because without it the radical chain would in principle continue indefinitely, and these combination steps are what eventually consume the reactive radical species and bring the reaction to completion.

Why is the formation of a small amount of ethane considered evidence for the free radical mechanism?

Ethane can only form if two separate methyl radicals happen to collide and combine directly with each other, which is a distinct, rare termination pathway with no other plausible explanation in this reaction system; because this particular product cannot be explained by any purely ionic or molecular mechanism, its detection, even in trace amounts, is taken as direct experimental evidence that free methyl radicals genuinely exist as intermediates during the reaction.

Explain the mechanism of electrophilic addition in alkenes, using the reaction of ethene with bromine and the reaction of propene with hydrogen bromide as examples, and explain how Markovnikov's rule follows from carbocation stability.

Why does a non-polar bromine molecule act as an electrophile when it approaches an alkene's double bond?

As a non-polar Br_2 molecule approaches the electron-rich $\text{C}=\text{C}$ double bond, the high electron density of the double bond repels the shared electron pair within the $\text{Br}-\text{Br}$ bond away from the nearer bromine atom; this induces a temporary dipole in which the nearer bromine atom becomes slightly positively charged, allowing it to act as an electrophile even though the isolated Br_2 molecule itself has no permanent polarity.



What intermediate forms when bromine adds to ethene, and how is the final product formed?

The pi electrons of the double bond attack the partially positive bromine atom, forming a new C-Br bond and generating a carbocation intermediate on the other alkene carbon, while a free bromide ion (Br^-) is released; this bromide ion then acts as a nucleophile, attacking the carbocation to form the second C-Br bond and complete the addition product, 1,2-dibromoethane.

What is the first step when propene reacts with HBr, and what carbocation does it form?

The pi electrons of propene's $\text{C}=\text{C}$ double bond attack the partially positive hydrogen atom of HBr, breaking the H-Br bond heterolytically to release a bromide ion; hydrogen adds to the terminal carbon (the one already bearing more hydrogens), which places the resulting positive charge on the middle carbon, forming a secondary carbocation rather than a primary one.

Why does the reaction favour formation of the secondary carbocation over the primary carbocation?

The middle carbon of the secondary carbocation is directly bonded to two alkyl (methyl and ethyl-fragment) groups, each of which donates electron density toward the positive charge through their +I inductive effect, spreading out and reducing the effective positive charge; a primary carbocation, formed if hydrogen instead added to the middle carbon, would have only one such electron-donating alkyl group and would therefore be markedly less stable and less likely to form.

How does this carbocation stability preference explain Markovnikov's rule and the major product formed?

Because the reaction proceeds through whichever carbocation intermediate is more stable, and the secondary carbocation is favoured for the reasons above, the bromide ion then attacks this more abundant secondary carbocation to give 2-bromopropane as the major product, with only a small amount of 1-bromopropane formed via the less-favoured primary carbocation pathway; this outcome, in which the negative part of the reagent ends up on the carbon that already had fewer hydrogens, is exactly what Markovnikov's rule predicts.



Multiple Choice Questions (MCQs)

An alkane has the molecular formula C_6H_{14} . Which classification correctly describes it?

- A. Aromatic hydrocarbon
- B. Aliphatic, saturated hydrocarbon
- C. Aliphatic, unsaturated hydrocarbon
- D. Cyclic hydrocarbon

Answer: B. Aliphatic, saturated hydrocarbon

Explanation: C_6H_{14} fits the general alkane formula C_nH_{2n+2} , so it is a saturated hydrocarbon; since it is not based on benzene, it belongs to the aliphatic (not aromatic) class.

What products form when a covalent bond undergoes homolytic fission?

- A. Two oppositely charged ions
- B. A cation and an anion
- C. Two free radicals
- D. A carbene and a carbanion

Answer: C. Two free radicals

Explanation: Homolytic fission breaks a bond evenly, with each atom retaining one electron of the originally shared pair, producing two free radicals, each bearing an unpaired electron.

Which step in free radical halogenation of an alkane involves breaking the halogen-halogen bond using UV light?

- A. Propagation
- B. Initiation
- C. Termination
- D. Substitution

Answer: B. Initiation

Explanation: The initiation step is the first step of the mechanism, in which UV light supplies the energy needed to homolytically break the halogen-halogen bond, generating the initial halogen radicals.

Which carbocation is the most stable, according to the inductive effect of alkyl groups?



- A. Methyl carbocation
- B. Primary (1 degree) carbocation
- C. Secondary (2 degree) carbocation
- D. Tertiary (3 degree) carbocation

Answer: D. Tertiary (3 degree) carbocation

Explanation: A tertiary carbocation is bonded to three alkyl groups, each donating electron density through the +I inductive effect, giving it the greatest stability among the four carbocation types.

Ethene reacts with HBr to form bromoethane. What type of intermediate forms during this reaction?

- A. A free radical
- B. A carbanion
- C. A carbocation
- D. An epoxide

Answer: C. A carbocation

Explanation: The pi electrons of the C=C double bond attack the partially positive hydrogen of HBr, forming a carbocation intermediate that is subsequently attacked by the bromide ion to complete the addition.

According to Markovnikov's rule, when HBr adds to propene, the major product is:

- A. 1-Bromopropane, because hydrogen adds to the more substituted carbon
- B. 2-Bromopropane, because the negative part of the reagent adds to the carbon with fewer hydrogens
- C. 1-Bromopropane, because bromide is a strong nucleophile
- D. A 50:50 mixture of 1-bromopropane and 2-bromopropane

Answer: B. 2-Bromopropane, because the negative part of the reagent adds to the carbon with fewer hydrogens

Explanation: Markovnikov's rule states that the negative part of the reagent (Br-) attaches to the double-bonded carbon bearing fewer hydrogens, which in propene is the middle carbon, giving 2-bromopropane as the major product via the more stable secondary carbocation.

Which of the following reactions of ethene converts it directly into a three-membered cyclic ether?



- A. Hydrogenation
- B. Ozonolysis
- C. Epoxidation
- D. Halohydrate

Answer: C. Epoxidation

Explanation: Epoxidation of an alkene produces an oxygen-containing three-membered cyclic ether called an epoxide, distinct from ozonolysis (which cleaves the double bond) and hydrogenation (which saturates it).

Which pair of compounds is an example of chain isomerism?

- A. Ethanol and methoxymethane
- B. n-Butane and isobutane (2-methylpropane)
- C. 1-Chloropropane and 2-chloropropane
- D. But-1-ene and but-2-ene

Answer: B. n-Butane and isobutane (2-methylpropane)

Explanation: Chain isomerism arises from differences in the branching of the carbon chain while keeping the same molecular formula; n-butane and isobutane both have the formula C_4H_{10} but differ in chain branching.

1,3-Butadiene is described as a conjugated diene because:

- A. Its two double bonds are separated by two single bonds
- B. Its two double bonds are separated by exactly one single bond, allowing p-orbital overlap
- C. It contains a triple bond adjacent to a double bond
- D. Its double bonds are on non-adjacent carbons with no p-orbital overlap possible

Answer: B. Its two double bonds are separated by exactly one single bond, allowing p-orbital overlap

Explanation: A conjugated diene has its two $C=C$ double bonds separated by exactly one single bond, which allows the p-orbitals on three or more consecutive carbons to overlap and delocalize the pi electrons across the system.

Which of the following is classified as an organic reduction reaction?

- A. Combustion of ethane to CO_2 and H_2O
- B. Oxidation of ethanol to ethanoic acid using $K_2Cr_2O_7$
- C. Addition of H_2 across a $C=C$ double bond using a Ni catalyst
- D. Ozonolysis of an alkene using O_3



Answer: C. Addition of H_2 across a $C=C$ double bond using a Ni catalyst

Explanation: Organic reduction is generally recognized by the addition of hydrogen (or removal of oxygen); adding molecular hydrogen across a $C=C$ double bond in the presence of a nickel catalyst converts an alkene to a saturated alkane, which is a reduction reaction.

Quick Revision Summary

- Hydrocarbons = only C and H; divided into aliphatic (alkanes, cycloalkanes, alkenes, alkynes) and aromatic (benzene-based)
- Alkanes: C_nH_{2n+2} , saturated, tetrahedral (sp^3 , 109.5 degrees); named by longest chain + lowest locants + alphabetical substituents
- Alkanes are unreactive toward polar reagents: nearly non-polar C-H/C-C bonds, strong sigma bonds
- Free radical substitution (halogenation): initiation (UV breaks X-X homolytically) $\rightarrow$ propagation ($X\cdot + \text{alkane} \rightarrow \text{alkyl radical} + HX$; $\text{alkyl radical} + X_2 \rightarrow \text{haloalkane} + X\cdot$) $\rightarrow$ termination (radicals combine)
- Halogen reactivity: $F_2 > Cl_2 > Br_2 > I_2$ (I_2 too slow/reversible to substitute directly)
- Alkenes: C_nH_{2n} , unsaturated, $C=C$ from sp^2 carbons (120 degrees, planar); sigma + pi bond, pi bond weaker and more reactive
- Ethene preparation: dehydration of ethanol (conc. H_2SO_4 , 180C) or dehydrohalogenation of ethyl bromide (alcoholic KOH, heat)
- Carbocation stability: 3 degree $>$ 2 degree $>$ 1 degree $>$ methyl, due to +I (electron-donating) effect of alkyl groups; halogens show -I (electron-withdrawing) effect
- Electrophilic addition mechanism: electrophile (X^+) attacks $C=C \rightarrow$ carbocation intermediate $\rightarrow$ nucleophile (Y^-) attacks $\rightarrow$ addition product
- Markovnikov's rule: negative part of unsymmetrical reagent adds to the carbon with fewer hydrogens (via the more stable carbocation)
- Alkene reactions: halogenation, hydrohalogenation, hydrogenation (Ni/Pt catalyst), hydration (H_2SO_4 catalyst), halohydrin, epoxidation, ozonolysis, polymerization
- Conjugated dienes: two $C=C$ separated by one single bond, allowing p-orbital overlap and pi-electron delocalization, increasing stability



- Isomerism: same molecular formula, different structure; Structural (chain, position, functional group, metamerism, tautomerism) vs Stereoisomerism (geometrical, optical)
- Organic oxidation: adds O / removes H (e.g. combustion, $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation of alcohols); Organic reduction: adds H / removes O (e.g. hydrogenation, $\text{LiAlH}_4/\text{NaBH}_4$)

Exam Tips

- When naming a branched alkane, first find the longest continuous chain (it may not be drawn in a straight line), then number from whichever end gives the lowest locants to the substituents as a set
- Remember alkyl groups are always named by dropping '-ane' and adding '-yl' from the corresponding alkane, and are listed alphabetically in a name (ignoring di-, tri-, tetra- prefixes)
- For free radical mechanisms, always identify which step is initiation (bond-breaking by light/heat), which two steps are propagation (chain-sustaining, net atoms/radicals balance), and which is termination (radicals combine, chain ends)
- For alkene addition reactions, always draw the carbocation intermediate first and check which carbon it forms on -- the more substituted (more stable) carbocation determines the major product under Markovnikov's rule
- Remember the $\text{C}=\text{C}$ double bond in alkenes consists of one sigma bond (strong, from head-on sp^2 orbital overlap) and one pi bond (weaker, from sideways p-orbital overlap) -- it is always the pi bond that breaks first during addition reactions
- When identifying isomerism type in an exam question, first check if molecular connectivity differs (structural isomerism, and if so which of the five subtypes) or if only spatial arrangement differs (stereoisomerism)



Chapter 12: Nitrogen and Sulfur

Nitrogen, a group 15 element making up most of Earth's atmosphere, is remarkably unreactive because of its strong, non-polar N-N triple bond, which requires a very large amount of energy to break; despite this inertness, nitrogen forms the important base ammonia through the Haber-Bosch process, and a range of oxides (NO, N₂O, NO₂, N₂O₄, N₂O₅) that arise from both natural and human sources and play a central role in forming photochemical smog and peroxyacyl nitrates (PANs). Catalytic converters use precious metal catalysts to remove these harmful nitrogen oxides from vehicle exhaust, while the natural nitrogen cycle continually interconverts ammonia, nitrite, nitrate, and nitrogen gas through nitrification and denitrification.

Sulfur, a group 16 chalcogen, is similarly unreactive at room temperature, forming stable S₈ crown-shaped rings through catenation rather than double bonds, and displaying a range of oxidation states from -2 to +6 whose relative stability depends on pH, temperature, and the surrounding chemical environment. Sulfur and its compounds have extensive industrial uses, from vulcanizing rubber and manufacturing fertilizers and gunpowder to serving as the backbone of countless drugs, dyes, and fragrances, but by far its most important industrial application is the manufacture of sulfuric acid via the Contact Process, an acid whose versatile chemical properties as an autoionizing solvent, strong acid, powerful dehydrating agent, and moderate oxidizing agent make it one of the most widely used industrial chemicals in the world.

Learning Objectives

- Explain the lack of reactivity of nitrogen due to its triple bond strength and lack of polarity
- Describe the basicity of ammonia using the Bronsted-Lowry theory, and identify the structure of the ammonium ion and how it forms through an acid-base reaction
- Describe how ammonia can be displaced from ammonium salts through an acid-base reaction



- Describe natural and man-made occurrences of oxides of nitrogen and their catalytic removal from exhaust gases
- Explain the role of NO and NO₂ in the formation of photochemical smog, specifically their reaction with unburned hydrocarbons to form peroxyacetyl nitrate (PAN)
- Differentiate between nitrification and denitrification
- Explain the lack of reactivity of sulfur, with reference to its bonding and the stability of its compounds
- Describe the different oxidation states of sulfur and their relative stability
- Describe the properties, production, and industrial applications of sulfuric acid
- Describe the chemical reactions and processes involving sulfur, and explain the uses of sulfur compounds in industry, everyday life, and organic synthesis

Key Concepts

12.1 Reactivity of Nitrogen (N₂)

Nitrogen (group 15, electronic configuration [He] 2s² 2p³) is obtained industrially by cooling air until it liquefies, and in the laboratory by gently heating ammonium nitrite solution. Nitrogen's low reactivity comes from two factors: its small, symmetrical electron cloud lets the two atoms form a triple bond with a very high bond enthalpy of +944 kJ/mol, requiring a large energy input to break; and since both atoms are identical, the bond is completely non-polar, with the three bonding electron pairs shared perfectly equally. This inertness makes nitrogen useful for diluting oxygen in the air (preventing every spark from causing fire), blanketing flammable cargo such as hydrocarbons or edible oils, and providing an inert atmosphere for laboratory reactions.

12.2 Ammonia (NH₃): Basicity, Structure, and Preparation

Ammonia, prepared industrially by the Haber-Bosch process ($\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$), behaves as a Bronsted-Lowry base by accepting a proton from an acid to form the ammonium ion, $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$. Dissolved in water it forms ammonium hydroxide, establishing the equilibrium $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, with a small basicity constant $K_b = 1.8 \times 10^{-5}$, meaning ammonia is a weak base because this equilibrium lies far to the left.



The ammonia molecule is pyramidal because of nitrogen's lone pair, but when that lone pair is used to accept a proton and form the ammonium ion, the resulting NH_4^+ ion becomes tetrahedral, with all four N-H bonds equal in length and strength. In the laboratory, ammonia gas is prepared by heating an ammonium salt such as ammonium chloride with a base like calcium hydroxide: $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{NH}_3$; in this acid-base reaction, NH_4^+ acts as an acid (donating H^+) and OH^- acts as a base (accepting H^+), and the released ammonia, identifiable by its pungent smell and its ability to turn moist red litmus paper blue, is used as a standard test for ammonium ions in salt analysis.

12.3 Oxides of Nitrogen

Nitrogen forms a series of oxides, NO , N_2O , NO_2 , N_2O_4 , and N_2O_5 , with oxidation states ranging from +1 to +5; N_2O_4 and N_2O_5 both decay quickly to other oxides, and NO together with NO_2 are collectively known as NO_x . Nitrous oxide (N_2O , laughing gas, +1 state) is a colourless, water-soluble, sweet-smelling gas used as a dental anaesthetic and whipped-cream propellant; nitric oxide (NO , +2 state) is a paramagnetic, slightly soluble gas that acts as a biochemical messenger (lowering blood pressure) and is both an oxidizing and reducing agent; and nitrogen dioxide (NO_2 , +4 state) is a reddish-brown, paramagnetic gas that reacts with water to form nitric and nitrous acids, and cools reversibly to colourless dinitrogen tetroxide (N_2O_4), used in rocket propellants and the Ostwald process for making nitric acid.

12.4 Sources of Oxides of Nitrogen

Natural sources of NO_x include lightning (which fuses atmospheric N_2 and O_2 directly into NO), volcanic eruptions, forest fires, and denitrifying soil bacteria that produce N_2O . Anthropogenic (human-made) sources are dominated by the combustion of fossil fuels in vehicles and power plants, along with chemical plants, biomass burning, and welding.

12.5 Role of NO and NO_2 in Smog and PAN Formation

Photochemical (Los Angeles-type) smog forms when NO_x and volatile organic compounds (VOCs) react in sunlight, producing an oxidizing mixture of



photochemical oxidants including NO₂, ozone, and peroxyacyl nitrates (PANs); it is becoming more common than classical (London-type) smog as NO_x emissions rise. The formation sequence begins with N₂ and O₂ reacting (from combustion or lightning) to form NO, which is further oxidized by O₂ to NO₂; sunlight then photolyzes NO₂ back into NO plus an oxygen atom, which combines with O₂ to form ground-level ozone (O₃), the main oxidant driving the rest of the smog chemistry.

Peroxyacyl nitrates (PANs) form when ozone oxidizes a hydrocarbon to an aldehyde, which reacts with a hydroxyl radical to form an acyl radical; this acyl radical then reacts with O₂ to form a peroxyacyl radical, which finally reacts with NO₂ to form the peroxyacyl nitrate itself, RC(O)OONO₂ (in peroxyacetyl nitrate specifically, R = CH₃). This mechanism explains directly why NO and NO₂, together with unburned hydrocarbons and sunlight, are essential ingredients of photochemical smog.

12.6 Catalytic Converters

A catalytic converter is a ceramic or metallic honeycomb structure coated with a high-surface-area alumina layer, on which the precious metals platinum, palladium, and rhodium are dispersed; these expensive metals can later be recycled. The converter catalyzes three simultaneous redox reactions to remove harmful exhaust gases: a reduction reaction converting NO and CO into N₂ and CO₂ ($2\text{NO} + 2\text{CO} \xrightarrow{\text{Pt/Rh}} \text{N}_2 + 2\text{CO}_2$), and two oxidation reactions converting remaining CO and unburned hydrocarbons into CO₂ and water ($2\text{CO} + \text{O}_2 \xrightarrow{\text{Pt/Pd}} 2\text{CO}_2$; $2\text{C}_2\text{H}_4 + 6\text{O}_2 \xrightarrow{\text{Pt/Pd}} 4\text{CO}_2 + 4\text{H}_2\text{O}$), together turning three harmful pollutants into far less harmful products.

12.7 Nitrification and Denitrification

Nitrification and denitrification are complementary phases of the nitrogen cycle. Nitrification converts ammonium (NH₄⁺) into nitrite (NO₂⁻) and then nitrate (NO₃⁻), carried out by nitrifying bacteria under aerobic conditions (pH 6.5-8.0, 20-30 degrees C); plants absorb these nitrites and nitrates for nutrition since they cannot assimilate atmospheric nitrogen directly. Denitrification reverses this, converting nitrate back through nitrite, NO, and N₂O into N₂ gas released to the atmosphere, carried out by denitrifying bacteria under anaerobic conditions



(pH 7.0-9.0, 26-38 degrees C); it is important in wastewater treatment and, together with the Anammox process (which oxidizes NH_4^+ with NO_2^- to form N_2 gas directly), supports healthy aquatic ecosystems.

12.8 Sulfur: Physical Properties, Reactivity, and Oxidation States

Sulfur (group 16, the chalcogen family, $[\text{Ne}] 3s^2 3p^4$) usually forms single S-S bonds rather than double bonds because of poor p-orbital overlap between larger sulfur atoms, leading it to catenate into larger structures; its most common form is S_8 , a crown-shaped ring of eight sulfur atoms. Sulfur displays oxidation states of -2, 0, +2, +4, and +6, determined by how many unpaired electrons are available: unlike oxygen, sulfur's third shell has accessible d-orbitals, allowing it to become excited into states with 4 or 6 unpaired electrons and giving oxidation states of +4 (as in SO_2) and +6 (as in SO_3 , which requires more energy to form).

The relative stability of sulfur's oxidation states depends on several factors: under acidic conditions, reduced forms like H_2S (-2) are more stable, while under basic or neutral conditions, oxidized forms like SO_4^{2-} (+6) are more stable in water; thermodynamically, sulfur(+6) as SO_3 is the most stable form, but kinetic limitations often prevent it from forming readily at ordinary temperatures, making sulfur(+4) as SO_2 the more commonly observed form; the nature of the compound and its bonding environment matters too, since SO_4^{2-} is kinetically stabilized in acidic environments by strong O-S bonds; and catalysts, such as vanadium in the Contact Process, can significantly speed up the formation of a particular oxidation state such as SO_3 .

12.9 Reactions and Uses of Sulfur

Sulfur is unreactive toward water, dilute non-oxidizing acids, and noble gases under normal conditions, but combines readily with many elements: it burns in air with a blue flame to form SO_2 (with SO_3 requiring higher temperature and a catalyst), can be oxidized by nitric acid to H_2SO_4 and NO_2 , acts as an oxidizing agent toward less electronegative metals such as silver, mercury, and copper to tarnish them with a metal sulfide coating, converts cyanide into thiocyanate (a pseudohalide), and reacts directly with fluorine to form SF_6 (an unreactive gas used as an electrical insulator) or with chlorine to form S_2Cl_2 and then SCl_2 .



Industrially and domestically, sulfur is used to vulcanize rubber by forming disulfide (S-S) cross-links between polymer chains, which strengthens the rubber; as a soil nutrient supplied via ammonium sulfate, elemental sulfur, sulfur-coated urea, or gypsum fertilizer; and as an ingredient in gunpowder (a blend of 75% potassium nitrate, 15% charcoal, and 10% sulfur, in which nitrate is the oxidizer, charcoal the main fuel, and sulfur an additional fast-burning fuel). Sulfur is also central to organic synthesis, forming carbon-sulfur bonds in thiols, thioethers, sulfoxides, and sulfones found in sulfa drugs such as penicillins and the sulfoxide-containing drug omeprazole, in sulfur dyes made by thionating nitro- or amino-containing organic compounds, and in mercaptans and thiols used as odorants (giving natural gas its smell) and fragrances.

12.10 Sulfuric Acid: Contact Process, Properties, and Applications

About 85% of sulfur produced is used to manufacture sulfuric acid (H_2SO_4), a tetrahedral molecule with two S-O and two S=O bonds, via the Contact Process. The process begins by burning molten sulfur or roasting iron pyrite in excess air to form SO_2 ; if pyrite is the source, the gas is purified (an arsenic purifier using gelatinous $\text{Fe}(\text{OH})_3$ removes contaminating As_2O_3); the purified SO_2 and preheated air (420-450 degrees C, 1-2 atm) then pass over a vanadium pentoxide (V_2O_5) catalyst in the contact tower, where $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3$ (V_2O_5 first oxidizes SO_2 to SO_3 while being reduced to V_2O_4 , then is reoxidized back to V_2O_5 by O_2); finally, in the absorption tower, SO_3 is dissolved in recirculating 98.5% sulfuric acid (not water directly, since that reaction is dangerously exothermic and produces acid mist rather than liquid) to form oleum (fuming sulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$), which is then diluted with water to give concentrated H_2SO_4 of adjustable strength.

Sulfuric acid is a colourless, odourless, hygroscopic, highly corrosive, and very polar liquid; it self-ionizes (autoprotolysis) and is a strong acid in its first ionization ($\text{pK}_{\text{a}1} = -2$) but a much weaker acid in its second ionization to give sulfate ($\text{pK}_{\text{a}2} = 1.92$, as HSO_4^-). Concentrated sulfuric acid is a powerful dehydrating agent, removing water from sucrose, starch, wood, and paper to leave carbon, and dehydrating ethanol to ethene; it reacts with NaCl to release HCl gas, reacts with reactive metals (above hydrogen in the electrochemical series) in dilute form to release H_2 gas, and in hot concentrated form acts as a



moderate oxidizing agent capable of oxidizing metals like copper, releasing SO_2 . Sulfuric acid's major industrial uses include fertilizer manufacture (digesting phosphate rock and reacting with ammonia to make ammonium sulfate), metal extraction, catalysis in oil and coal refining and polymer manufacture, paper production, pesticide and dye manufacture, explosive nitration (TNT, nitroglycerine), sugar processing, TiO_2 pigment production, industrial gas drying, and lead-acid batteries, making it one of the most widely produced industrial chemicals in the world.

Important Definitions

Why is nitrogen gas (N_2) so unreactive?

Because its two atoms are held together by a strong, non-polar triple bond with a bond enthalpy of +944 kJ/mol, requiring a very large amount of energy to break before new bonds can form.

What is the basicity constant (K_b) of ammonia?

$K_b = 1.8 \times 10^{-5}$, a small value that shows ammonia is a weak base because its equilibrium with water lies far toward the unreacted ammonia side.

What is the shape of the ammonium ion (NH_4^+), and why does it differ from ammonia's shape?

The ammonium ion is tetrahedral, with four equal N-H bonds; this differs from ammonia's pyramidal shape because nitrogen's lone pair, which caused the pyramidal distortion in NH_3 , is used to form the fourth N-H bond in NH_4^+ .

What are NO_x gases?

The collective name for nitric oxide (NO) and nitrogen dioxide (NO_2), the two nitrogen oxides most responsible for photochemical smog and related atmospheric pollution.

What is a catalytic converter?

A ceramic or metallic honeycomb device coated with platinum, palladium, and rhodium on a high-surface-area alumina layer, which catalyzes redox reactions converting harmful exhaust gases (CO , NO , hydrocarbons) into CO_2 , N_2 , and water.

What is nitrification?



The conversion of ammonium (NH_4^+) into nitrite (NO_2^-) and then nitrate (NO_3^-) by nitrifying bacteria under aerobic conditions, making nitrogen available for plant nutrition.

What is denitrification?

The conversion of nitrate (NO_3^-) back through nitrite, NO, and N_2O into nitrogen gas (N_2), carried out by denitrifying bacteria under anaerobic conditions.

Why does sulfur form S8 rings instead of double bonds like oxygen?

Sulfur atoms are larger than oxygen atoms, giving poorer p-orbital overlap for pi bonding, so sulfur instead catenates through single S-S bonds, forming the crown-shaped eight-membered S8 ring as its most stable structure.

What is oleum?

Fuming sulfuric acid, formed by dissolving sulfur trioxide (SO_3) in concentrated (98.5%) sulfuric acid; it is diluted with water in a controlled way to produce concentrated sulfuric acid of adjustable strength.

Why is sulfuric acid described as a 'king of chemicals'?

Because its production and consumption are used as an indicator of a country's industrial progress, reflecting its enormous range of uses across fertilizers, metal extraction, catalysis, paper, dyes, explosives, food processing, pigments, gas drying, and batteries.

Key Facts and Relations

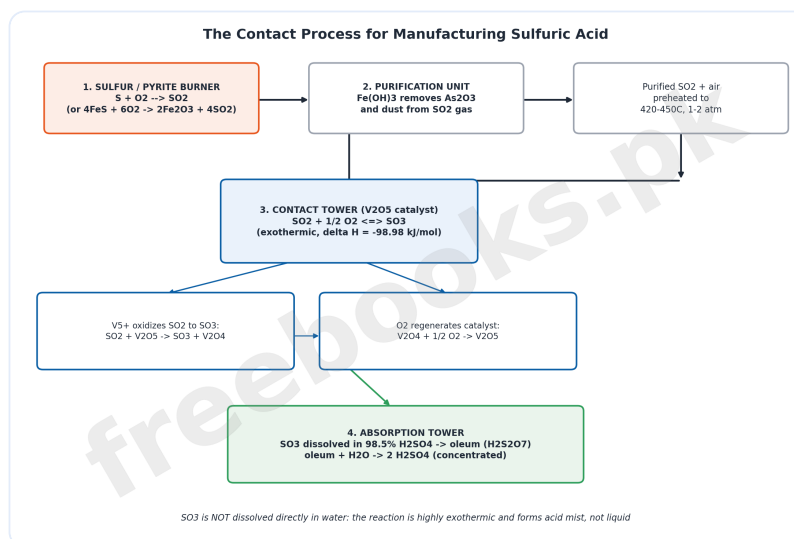
Topic	Key Fact / Relation
N_2 bond enthalpy	+944 kJ/mol (very strong, non-polar triple bond)
Basicity of ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, $K_b = 1.8 \times 10^{-5}$
Ammonia from ammonium salt	$2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{NH}_3$
Photochemical smog: NO/NO ₂ /O ₃ formation	$\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$; $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$; $\text{NO}_2 \xrightarrow{-h\nu} \text{NO} + \text{O}\cdot$; $\text{O}\cdot + \text{O}_2 \rightarrow \text{O}_3$
PAN formation	$\text{RCO}_3\cdot + \text{NO}_2 \rightarrow \text{RC}(\text{O})\text{OONO}_2$ (peroxyacyl nitrate)
Catalytic converter (reduction)	$2\text{NO} + 2\text{CO} \xrightarrow{\text{Pt/Rh}} \text{N}_2 + 2\text{CO}_2$



Topic	Key Fact / Relation
Sulfur oxidation states	-2, 0, +2, +4, +6 (d-orbitals allow +4 and +6 via excitation)
Contact Process (SO ₂ to SO ₃)	$\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3$ (V ₂ O ₅ catalyst), $\Delta H = -98.98 \text{ kJ/mol}$
Absorption tower (oleum)	$\text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow \text{H}_2\text{S}_2\text{O}_7$ (oleum); $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$
Sulfuric acid ionization	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-$ ($\text{pK}_{\text{a}1} = -2$); $\text{HSO}_4^- \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$ ($\text{pK}_{\text{a}2} = 1.92$)

Diagrams

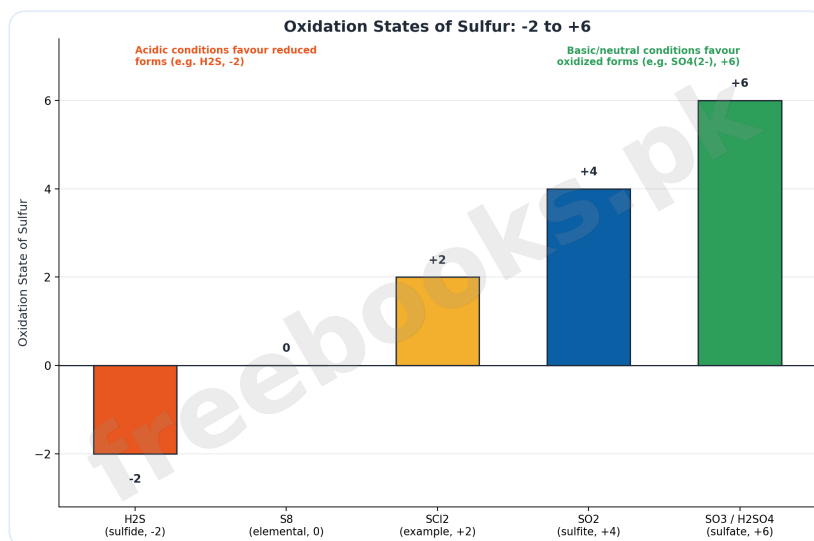
The Contact Process for Manufacturing Sulfuric Acid: A flow diagram of the four stages of the Contact Process: the sulfur/pyrite burner, purification unit, contact tower with V₂O₅ catalyst regeneration cycle, and absorption tower producing oleum and concentrated sulfuric acid



The Contact Process for Manufacturing Sulfuric Acid

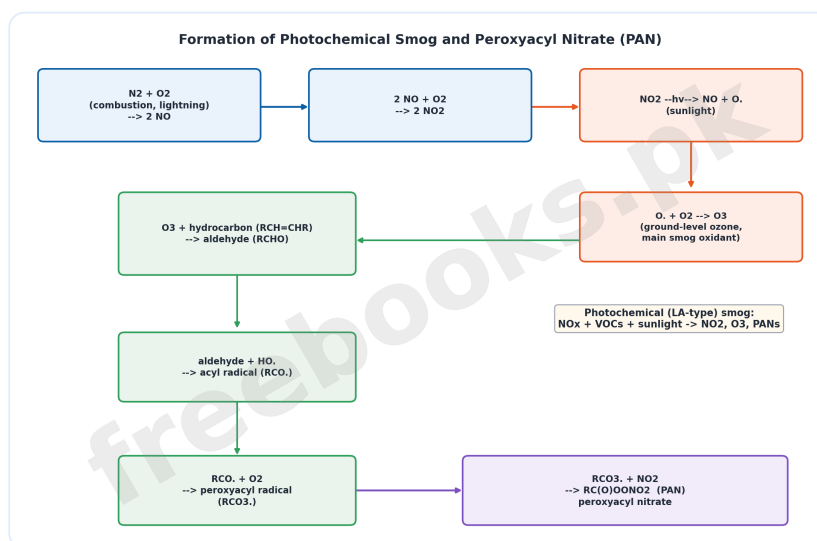
Oxidation States of Sulfur: A bar chart showing sulfur's oxidation states from -2 (H₂S) to +6 (SO₃/H₂SO₄), illustrating how acidic conditions favour reduced forms and basic or neutral conditions favour oxidized forms





Oxidation States of Sulfur

Formation of Photochemical Smog and Peroxyacyl Nitrate (PAN): A step-by-step flow diagram showing how NO , NO_2 , and ground-level ozone form from nitrogen and oxygen in sunlight, and how ozone then reacts with hydrocarbons through a series of radical intermediates to form PAN



Formation of Photochemical Smog and Peroxyacyl Nitrate (PAN)

Short Questions & Answers

Why is nitrogen gas used to create an inert atmosphere for storing flammable cargo such as hydrocarbons and edible oils?

Nitrogen's strong, non-polar triple bond makes it extremely unreactive under ordinary conditions, so it does not support combustion or react with the stored material; blanketing flammable cargo with nitrogen displaces oxygen and



moisture from the storage space, removing the conditions needed for a fire or oxidative spoilage to start.

Why is ammonia classified as a weak base rather than a strong base?

When ammonia dissolves in water it establishes the equilibrium $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$, but this equilibrium lies far toward the left, as reflected in its small basicity constant, $K_b = 1.8 \times 10^{-5}$; because only a small fraction of dissolved ammonia molecules actually accept a proton to form ammonium and hydroxide ions at any given time, ammonia solutions are only weakly basic.

Why does the ammonium ion (NH_4^+) have a tetrahedral shape while the ammonia molecule (NH_3) is pyramidal?

Ammonia's shape is pyramidal because nitrogen's lone pair of electrons occupies one of the four positions around the nitrogen atom, distorting the molecule away from a symmetrical shape; when this lone pair is used to accept a proton and form a fourth N-H bond in the ammonium ion, all four positions around nitrogen become equivalent bonding pairs, giving the ion a fully symmetrical tetrahedral shape.

Why is heating an ammonium salt with a base used as a standard test for ammonium ions in salt analysis?

This acid-base reaction reliably displaces ammonia gas from any ammonium salt, and ammonia gas has two easily observable diagnostic properties: a strong, distinctive pungent smell, and the ability to turn moistened red litmus paper blue because of its basicity; the simultaneous appearance of both signs upon heating a suspected ammonium compound with a base provides clear, unambiguous confirmation of ammonium's presence.

Why does the conversion of NO and CO into N_2 and CO_2 in a catalytic converter count as a reduction reaction?

In the reaction $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$, the nitrogen in NO, which starts with a positive oxidation state, ends up in N_2 with an oxidation state of zero, meaning nitrogen has gained electrons and been reduced; this reduction of NO to harmless N_2 gas is precisely the transformation the catalytic converter's platinum/rhodium catalyst is designed to promote.

Why does sulfur typically form single S-S bonds and catenate into rings like S_8 , rather than forming double bonds the way oxygen does in O_2 ?



Sulfur atoms are considerably larger than oxygen atoms, which weakens the sideways overlap of their p-orbitals needed to form a strong pi bond; because this poor orbital overlap makes double-bond formation energetically unfavourable for sulfur, it instead forms a series of single S-S sigma bonds, catenating into stable ring structures such as the eight-membered crown-shaped S₈ molecule.

Why are reduced sulfur species like H₂S more stable under acidic conditions, while oxidized species like SO₄²⁻ are more stable under basic or neutral conditions?

The relative stability of different sulfur oxidation states in water depends strongly on pH, because the availability of protons and hydroxide ions shifts the equilibria between sulfur species; under acidic conditions, an abundance of protons favours the reduced, less oxygenated form (H₂S, -2 state), while under basic or neutral conditions, favourable conditions for the highly oxygenated sulfate ion make SO₄²⁻ (+6 state) the thermodynamically preferred species.

Why is sulfur trioxide not dissolved directly in water during the Contact Process?

The reaction between SO₃ and water is extremely exothermic, and rather than forming a manageable liquid solution, the heat released causes the sulfuric acid product to form as a fine, difficult-to-collect acidic mist or vapour instead; to avoid this problem, SO₃ is instead dissolved in recirculating concentrated (98.5%) sulfuric acid to form oleum, which can then be safely and controllably diluted with water to give concentrated sulfuric acid.

Why is hot, concentrated sulfuric acid able to oxidize copper, even though sulfuric acid is not generally regarded as a strong oxidizing agent?

The sulfate ion (SO₄²⁻) itself is only weakly oxidizing because of its high stability, which is why sulfuric acid is not classified as a typical strong oxidizing agent; however, under hot and concentrated conditions, the high temperature, high concentration of protons, and generation of nascent oxygen combine to give the acid enough oxidizing power to oxidize a moderately unreactive metal like copper, releasing SO₂ gas in the process.

Why is concentrated sulfuric acid effective at dehydrating sucrose to leave behind a black carbon residue?



Concentrated sulfuric acid is strongly hygroscopic and has a powerful chemical affinity for water molecules; when applied to sucrose, it forcibly removes the hydrogen and oxygen atoms from the sugar molecule in the same 2:1 ratio as water, releasing them as steam and leaving behind only the carbon skeleton of the original sucrose molecule as a black, porous solid.

Long Questions & Answers

Explain how oxides of nitrogen contribute to the formation of photochemical smog and peroxyacyl nitrates (PANs), describing the full reaction sequence from nitrogen and oxygen to the final PAN product.

How does nitric oxide (NO) first form in the atmosphere, and how is it converted to nitrogen dioxide (NO₂)?

Nitric oxide forms when atmospheric nitrogen and oxygen react at the high temperatures generated by combustion in vehicle engines and power plants, or by lightning strikes, via $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$; this NO is then further oxidized by more atmospheric oxygen, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, converting it into the reddish-brown nitrogen dioxide that gives photochemical smog its characteristic haze.

How does sunlight convert NO₂ into ground-level ozone (O₃)?

Sunlight supplies enough energy to photolyze (break apart) the NO₂ molecule, $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}\cdot$, regenerating NO and releasing a highly reactive oxygen atom; this oxygen atom immediately combines with molecular oxygen in the air, $\text{O}\cdot + \text{O}_2 \rightarrow \text{O}_3$, producing ground-level ozone, which is itself a major component and oxidant of photochemical smog.

How does ozone initiate the formation of an aldehyde from an unburned hydrocarbon?

Ground-level ozone is highly reactive and readily attacks the carbon-carbon double bonds present in unburned volatile organic compounds (VOCs) released from vehicle exhaust and other sources, oxidatively cleaving the hydrocarbon;



this oxidation converts the hydrocarbon into a smaller aldehyde molecule (RCHO), the first organic intermediate on the pathway toward PAN formation.

What sequence of radical intermediates leads from the aldehyde to the peroxyacyl radical?

The aldehyde reacts with a hydroxyl radical (HO.), a highly reactive species present in the atmosphere, to form an acyl radical (RCO.); this acyl radical then reacts rapidly with molecular oxygen to form a peroxyacyl radical (RCO₃.), the final reactive intermediate before PAN itself is formed.

How is the final PAN molecule formed, and why does this make NO_x central to PAN formation?

The peroxyacyl radical reacts directly with nitrogen dioxide, $\text{RCO}_3\cdot + \text{NO}_2 \rightarrow \text{RC(O)OONO}_2$, to form the peroxyacyl nitrate (PAN) product; because NO₂ is required as the direct reactant in this final step, and NO/NO₂ are also essential to generating the ozone that starts the whole sequence, oxides of nitrogen are involved at multiple stages of PAN formation, making NO_x emissions a central driver of photochemical smog toxicity.

Describe the industrial production of sulfuric acid by the Contact Process, and explain how each stage is designed to maximize yield, purity, and safety.

What happens in the first stage of the Contact Process, and what determines which raw material is used?

The process begins by burning molten sulfur directly in air, $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$, or, if pyrite ore is the sulfur source instead, by roasting iron pyrite in excess air, $4\text{FeS} + 6\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$; either route produces the sulfur dioxide gas that is the essential starting material for the rest of the process.

Why is a purification unit needed when pyrite ore is used as the sulfur source, and how does it work?

SO₂ gas produced from roasting pyrite ore often contains contaminants such as dust particles, vapours, and arsenic oxide (As₂O₃), which can poison or reduce



the efficiency of the vanadium pentoxide catalyst used later in the process; an arsenic purifier containing gelatinous ferric hydroxide, $\text{Fe}(\text{OH})_3$, absorbs the arsenic oxide contaminant, $\text{As}_2\text{O}_3 + 2\text{Fe}(\text{OH})_3 \rightarrow 2\text{FeAsO}_3 + 3\text{H}_2\text{O}$, protecting the catalyst downstream.

How does the vanadium pentoxide (V_2O_5) catalyst convert SO_2 into SO_3 in the contact tower?

The catalyst works through a two-step redox cycle: first, V^{5+} in V_2O_5 oxidizes SO_2 to SO_3 while itself being reduced to V_2O_4 , $\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4$; then, atmospheric oxygen reoxidizes the V_2O_4 back to V_2O_5 , $\text{V}_2\text{O}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{V}_2\text{O}_5$, regenerating the catalyst so it can repeat the cycle indefinitely without being consumed.

Why is SO_3 not simply dissolved directly in water in the absorption tower?

Dissolving SO_3 directly in water is an extremely exothermic reaction that generates so much heat so quickly that the product forms as a fine, hard-to-collect corrosive acid mist rather than a controllable liquid solution; to avoid this hazard, SO_3 is instead dissolved in recirculating hot, concentrated (98.5%) sulfuric acid, a much safer and more controllable absorption medium.

How is oleum converted into usable concentrated sulfuric acid of a desired strength?

The SO_3 absorbed into concentrated sulfuric acid first forms oleum (fuming sulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$), via $\text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow \text{H}_2\text{S}_2\text{O}_7$; this oleum is then reacted with a carefully controlled, measured amount of water, $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$, which safely converts it into concentrated sulfuric acid, and by controlling how much water is added, the final concentration of the acid can be precisely adjusted to the desired industrial specification.

Multiple Choice Questions (MCQs)

What is the bond enthalpy of the N_2 triple bond, and why is this significant?

- A. +436 kJ/mol; it makes nitrogen moderately reactive
- B. +944 kJ/mol; it makes nitrogen highly unreactive



- C. +150 kJ/mol; nitrogen reacts readily at room temperature
- D. +944 kJ/mol; but nitrogen is still highly reactive due to polarity

Answer: B. +944 kJ/mol; it makes nitrogen highly unreactive

Explanation: The N_2 triple bond has a bond enthalpy of +944 kJ/mol, an unusually high value that requires a large energy input to break, which combined with the bond's non-polarity makes nitrogen gas highly unreactive under ordinary conditions.

Ammonia dissolves in water to form an equilibrium with ammonium and hydroxide ions. What does its small K_b value of 1.8×10^{-5} indicate?

- A. Ammonia is a strong base, fully ionized in water
- B. Ammonia is a weak base, with the equilibrium lying mostly toward unreacted NH_3
- C. Ammonia does not dissolve in water at all
- D. Ammonia is a strong acid in aqueous solution

Answer: B. Ammonia is a weak base, with the equilibrium lying mostly toward unreacted NH_3

Explanation: A small K_b value of 1.8×10^{-5} shows that only a small fraction of ammonia molecules accept a proton from water at equilibrium, meaning the equilibrium lies far toward the left (unreacted NH_3), which is the hallmark of a weak base.

What shape does the ammonium ion (NH_4^+) adopt, and why does it differ from ammonia's shape?

- A. Pyramidal, same as ammonia, since nitrogen's lone pair is unaffected
- B. Tetrahedral, because nitrogen's lone pair becomes a fourth bonding pair
- C. Linear, because the positive charge repels all bonding pairs into a line
- D. Trigonal planar, because nitrogen loses one bond upon ionization

Answer: B. Tetrahedral, because nitrogen's lone pair becomes a fourth bonding pair

Explanation: Ammonium is tetrahedral because nitrogen's lone pair, which caused ammonia's pyramidal shape, is used to form a fourth N-H bond upon accepting a proton, making all four positions around nitrogen equivalent bonding pairs.

Which nitrogen oxide is primarily responsible for reversibly dimerizing into a colourless form on cooling?



- A. N₂O (nitrous oxide)
- B. NO (nitric oxide)
- C. NO₂, which dimerizes to colourless N₂O₄ on cooling
- D. N₂O₅

Answer: C. NO₂, which dimerizes to colourless N₂O₄ on cooling

Explanation: Reddish-brown NO₂ gas reversibly dimerizes to colourless N₂O₄ on cooling (and reverts to NO₂ on heating), a property specifically described for this nitrogen oxide pair.

In a catalytic converter, which combination of reactions occurs simultaneously to remove harmful exhaust gases?

- A. Only reduction of NO to N₂
- B. Only oxidation of CO to CO₂
- C. Reduction of NO (with CO) to N₂, plus oxidation of remaining CO and hydrocarbons to CO₂ and water
- D. Neutralization of all exhaust gases with a base

Answer: C. Reduction of NO (with CO) to N₂, plus oxidation of remaining CO and hydrocarbons to CO₂ and water

Explanation: A three-way catalytic converter performs one reduction reaction ($2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$) and two oxidation reactions (oxidizing remaining CO and hydrocarbons to CO₂ and water) simultaneously, using platinum, palladium, and rhodium catalysts.

What is the key structural difference that explains why sulfur forms S₈ rings while oxygen forms O₂ with a double bond?

- A. Sulfur atoms are smaller, allowing stronger double bonds
- B. Sulfur atoms are larger, giving poorer p-orbital overlap that disfavors double bonds, favoring single-bond catenation instead
- C. Sulfur has no valence electrons available for pi bonding
- D. Oxygen cannot form single bonds under any conditions

Answer: B. Sulfur atoms are larger, giving poorer p-orbital overlap that disfavors double bonds, favoring single-bond catenation instead

Explanation: Sulfur's larger atomic size gives poorer p-orbital overlap for pi-bond formation compared to oxygen, so sulfur favors single S-S sigma bonds and catenates into ring structures like S₈ rather than forming a double-bonded diatomic molecule.



Which set of conditions is most likely to stabilize sulfate (SO_4^{2-} , +6 oxidation state) over hydrogen sulfide (H_2S , -2 oxidation state) in aqueous solution?

- A. Strongly acidic conditions
- B. Basic or neutral conditions
- C. Anhydrous, non-aqueous conditions only
- D. Very low temperature only, regardless of pH

Answer: B. Basic or neutral conditions

Explanation: Basic or neutral conditions favour the highly oxidized sulfate ion (SO_4^{2-} , +6), while acidic conditions favour the reduced hydrogen sulfide form (H_2S , -2), reflecting how pH shifts the relative stability of sulfur's oxidation states in water.

In the Contact Process, what is the role of the V_2O_5 catalyst in converting SO_2 to SO_3 ?

- A. It absorbs SO_3 directly into oleum
- B. It oxidizes SO_2 to SO_3 while being reduced to V_2O_4 , then is reoxidized by O_2 back to V_2O_5
- C. It reduces SO_3 back into SO_2 to control the reaction rate
- D. It purifies the gas stream of arsenic contaminants

Answer: B. It oxidizes SO_2 to SO_3 while being reduced to V_2O_4 , then is reoxidized by O_2 back to V_2O_5

Explanation: V_2O_5 works through a two-step cycle: V^{5+} first oxidizes SO_2 to SO_3 while itself being reduced to V_2O_4 , and atmospheric O_2 then reoxidizes V_2O_4 back to V_2O_5 , regenerating the catalyst for continued use.

Why is SO_3 dissolved in concentrated sulfuric acid rather than water during the absorption stage of the Contact Process?

- A. Water is too expensive to use industrially
- B. The reaction of SO_3 with water is highly exothermic and produces an unmanageable acid mist rather than a liquid
- C. SO_3 does not dissolve in water at all
- D. Sulfuric acid is a better solvent for SO_3 due to its higher boiling point alone

Answer: B. The reaction of SO_3 with water is highly exothermic and produces an unmanageable acid mist rather than a liquid

Explanation: Dissolving SO_3 directly in water releases so much heat so quickly



that a fine corrosive acid mist forms instead of a controllable liquid solution; dissolving SO₃ in concentrated sulfuric acid instead (forming oleum) avoids this hazard.

Which best describes sulfuric acid's oxidizing behaviour toward copper metal?

- A. Dilute sulfuric acid readily oxidizes copper at room temperature
- B. Sulfuric acid never oxidizes any metal under any conditions
- C. Hot, concentrated sulfuric acid can moderately oxidize copper, releasing SO₂, due to high temperature, high proton concentration, and nascent oxygen formation
- D. Copper spontaneously dissolves in cold, dilute sulfuric acid to release hydrogen gas

Answer: C. Hot, concentrated sulfuric acid can moderately oxidize copper, releasing SO₂, due to high temperature, high proton concentration, and nascent oxygen formation

Explanation: Although the stability of the sulfate ion generally makes sulfuric acid a weak oxidizing agent, hot concentrated sulfuric acid becomes a moderately strong oxidizing agent under these specific conditions, capable of oxidizing copper metal while itself being reduced to SO₂.

Quick Revision Summary

- Nitrogen (N₂): unreactive due to strong (+944 kJ/mol), non-polar N-N triple bond; used for inert atmospheres and blanketing flammable cargo
- Ammonia: Haber-Bosch process ($\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$); weak Bronsted-Lowry base, $K_b = 1.8 \times 10^{-5}$; pyramidal NH₃ vs tetrahedral NH₄⁺ (lone pair becomes bonding pair)
- Ammonia from ammonium salts: $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{NH}_3$ (acid-base reaction, standard test for NH₄⁺)
- Nitrogen oxides: N₂O (+1, laughing gas), NO (+2, paramagnetic), NO₂/N₂O₄ (+4, reddish-brown $\rightleftharpoons$ colourless); collectively NO_x = NO + NO₂
- NO_x sources: natural (lightning, volcanoes, forest fires, denitrifying bacteria) vs anthropogenic (vehicle/power plant combustion, chemical plants)
- Photochemical smog: NO_x + VOCs + sunlight $\rightarrow$ NO₂, O₃, PANs; sequence: $\text{N}_2 + \text{O}_2 \rightarrow \text{NO} \rightarrow \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 \rightarrow \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \rightarrow \text{O} + \text{O}_2 \rightarrow \text{O}_3$



- PAN formation: $\text{O}_3 + \text{hydrocarbon} \rightarrow \text{aldehyde} \rightarrow (+\text{HO}\cdot) \text{ acyl radical} \rightarrow (+\text{O}_2) \text{ peroxyacyl radical} \rightarrow (+\text{NO}_2) \text{ PAN}$
- Catalytic converter: Pt/Pd/Rh on alumina honeycomb; reduces $\text{NO} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2$, oxidizes CO and hydrocarbons to $\text{CO}_2 + \text{H}_2\text{O}$
- Nitrification ($\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$, aerobic) vs Denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$, anaerobic)
- Sulfur: group 16, forms S_8 crown rings via catenation (poor p-orbital overlap prevents $\text{S}=\text{S}$ double bonds)
- Sulfur oxidation states: -2, 0, +2, +4, +6 (d-orbitals allow excitation to +4/+6); acidic favours reduced forms, basic/neutral favours oxidized forms
- Contact Process: S/pyrite burner $\rightarrow$ purification ($\text{Fe}(\text{OH})_3$ removes As_2O_3) $\rightarrow$ contact tower (V_2O_5 catalyst, $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$) $\rightarrow$ absorption tower ($\text{SO}_3 + \text{conc. H}_2\text{SO}_4 \rightarrow \text{oleum} \rightarrow + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$)
- Sulfuric acid: strong acid ($\text{pK}_{\text{a}1}=-2$) but weak second ionization ($\text{pK}_{\text{a}2}=1.92$); autoionizes; powerful dehydrating agent; hot conc. acid is moderate oxidizer
- Sulfur uses: vulcanization (S-S cross-links), fertilizers, gunpowder ($\text{KNO}_3 + \text{C} + \text{S}$), sulfa drugs, dyes, fragrances; H_2SO_4 uses: fertilizers, metal extraction, catalysis, explosives, batteries

Exam Tips

- Remember nitrogen's inertness has TWO causes: high triple-bond enthalpy (kinetic/energy barrier) AND zero bond polarity (no partial charges to attract reagents) -- exam questions often ask for both
- For ammonium ion structure questions, always explain the shape change in terms of the lone pair becoming a bonding pair -- this is the key mechanistic detail examiners look for
- When tracing photochemical smog/PAN formation, write out the full sequence in order ($\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{O}_3 \rightarrow \text{aldehyde} \rightarrow \text{acyl radical} \rightarrow \text{peroxyacyl radical} \rightarrow \text{PAN}$) rather than jumping straight to the final equation
- For catalytic converter questions, remember it performs reduction AND oxidation simultaneously -- identify which gases are reduced (NO) and which are oxidized (CO, hydrocarbons)



- For sulfur oxidation state questions, connect the number of unpaired electrons (via excitation into d-orbitals) directly to the resulting oxidation state: 2 unpaired = +2, 4 unpaired = +4, 6 unpaired = +6
- For Contact Process questions, always name each of the four stages in order (burner, purification, contact tower, absorption tower) and state why SO_3 is absorbed into acid rather than water directly



Chapter 13: Halogens

The halogens (group 17: fluorine, chlorine, bromine, iodine, plus the rare radioactive astatine and tennessine) are a family of highly reactive, similar non-metals that exist as coloured diatomic molecules whose physical state, colour, and volatility change progressively down the group as increasing molecular size strengthens instantaneous dipole-induced dipole (London dispersion) forces. Their bond strength, oxidizing power as elements, and thermal stability as hydrogen halides all follow clear periodic trends (with fluorine as a notable exception in bond strength due to lone-pair repulsion), while halide ions show the opposite trend, becoming progressively stronger reducing agents from fluoride to iodide.

These trends underpin a set of classic qualitative tests: halide ions can be identified by the distinctive colours of their silver halide precipitates and by their differing solubility in aqueous ammonia, and by their differing behaviour with concentrated sulfuric acid, which ranges from simple fume formation with fluoride and chloride to full redox reactions with bromide and iodide. Chlorine additionally demonstrates disproportionation when reacted with cold versus hot sodium hydroxide, and its reaction with water to form the active disinfectant species HOCl and OCl⁻ underlies its widespread use in water purification.

Learning Objectives

- Describe the colours and trends in volatility of chlorine, bromine, and iodine
- Describe the trend in bond strength of halogen molecules
- Interpret the volatility of halogens in terms of instantaneous dipole-induced dipole forces
- Describe the relative reactivity of halogen elements as oxidizing agents
- Describe the reactions of halogens with hydrogen and explain their relative reactivity in these reactions
- Describe the relative thermal stabilities of hydrogen halides and explain these in terms of bond strength
- Describe the relative reactivity of halide ions as reducing agents



- Explain the reactions of halide ions with aqueous silver nitrate and concentrated sulfuric acid
- Describe the reactions of halides with aqueous silver ions followed by aqueous ammonia
- Interpret the reactions of chlorine with cold and hot aqueous sodium hydroxide as disproportionation reactions, and explain the use of chlorine in water purification

Key Concepts

13.1 The Halogen Family: Colours and Physical States

Group 17 elements are called halogens: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and the rare, radioactive astatine (At) and tennessine (Ts). Halogens exist as diatomic molecules (X_2) in all phases and form a group of very reactive, chemically similar non-metals; the name 'halogen' comes from Greek words meaning 'salt-forming'.

At room temperature, fluorine (pale yellow) and chlorine (greenish yellow) are gases, bromine (reddish-brown) is a volatile, corrosive, toxic liquid, and iodine (shiny greyish-black solid) sublimes directly to a violet vapour; colours darken progressively from chlorine to iodine due to changing light absorption from electron transitions within each halogen's molecules.

13.2 Volatility of the Halogens

Volatility decreases from chlorine to iodine (chlorine most volatile, iodine least) due to increasing molecular mass, increasing outer-shell size, and progressively stronger London dispersion (instantaneous dipole-induced dipole, id-id) forces down the group. Since halogens are non-polar, these id-id forces, which depend on molecular size, shape, and polarizability, govern their physical state: small, less polarizable molecules (F_2 , Cl_2) have weak id-id forces, low boiling points, and high volatility, while larger, more polarizable molecules (Br_2 , I_2) have strong id-id forces, high boiling points, and low volatility. Volatility is inversely related to boiling point: stronger intermolecular forces require more energy to separate molecules into the gas phase, giving a lower volatility.



13.3 Bond Strength of Halogen Molecules

Bond strength in halogens generally decreases down the group from chlorine to iodine, since increasing atomic size gives longer, weaker bonds; however, fluorine is an exception; despite fluorine's very high electronegativity, the F-F bond is relatively weak (156 kJ/mol) because fluorine's very small atomic size causes significant electron-electron repulsion between the lone pairs on the two bonded fluorine atoms, weakening the bond. Chlorine has the strongest X-X bond (243 kJ/mol) among the halogens, with bond energy then decreasing through bromine (193 kJ/mol) to iodine (151 kJ/mol).

13.4 Relative Reactivities of Halogens as Oxidizing Agents

All free halogens act as oxidizing agents toward metals and most non-metals, gaining electrons to form negative halide ions (e.g., $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$). Oxidizing power decreases down the group, $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$, reflecting each halogen's decreasing tendency to acquire an electron and form its halide ion; fluorine can oxidize and displace Cl^- , Br^- , and I^- from solution to their free halogens, chlorine can displace Br^- and I^- , bromine can displace only I^- , and iodine cannot displace any halide ion.

This oxidizing power trend correlates with standard electrode potentials $E^\circ(\text{X}_2/\text{X}^-)$, which become less positive from fluorine (+2.87 V) to iodine (+0.54 V), and depends on several combined factors: energy of dissociation, electron affinity, hydration energy of the resulting ion, and (for Br_2 and I_2) heat of vaporization; a halogen with low dissociation energy, high electron affinity, and high hydration energy of its ion will show high oxidizing power.

13.5 Reactions of Halogens with Hydrogen

Halogens react with hydrogen to form hydrogen halides, $\text{H}_2 + \text{X}_2 \rightarrow 2\text{HX}$, colourless gases that dissolve in water to form hydrohalic acids; reactivity toward hydrogen decreases down the group, $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. Fluorine reacts explosively with hydrogen even at low temperature and in the dark; chlorine reacts readily with hydrogen in UV light or with a spark; bromine reacts with hydrogen only on heating, in an exothermic reaction giving a strong hydrobromic



acid on dissolving; and iodine reacts with hydrogen only at high temperature with a catalyst, in a slow, reversible reaction.

13.6 Thermal Stability of Hydrogen Halides

Thermal stability of hydrogen halides decreases down the group, $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$, directly tracking their decreasing bond dissociation energies (H-F 569 kJ/mol, H-Cl 431 kJ/mol, H-Br 366 kJ/mol, H-I 299 kJ/mol). HF is the most stable because fluorine's high electronegativity and very small atomic radius give strong orbital overlap and a very strong H-F bond; as atomic radius increases down the group (Cl, then Br, then I), orbital overlap with hydrogen becomes progressively poorer, weakening the H-X bond and making the corresponding hydrogen halide progressively less thermally stable, with HI the least stable of the four.

13.7 Relative Reactivity of Halide Ions as Reducing Agents

Reducing power of halide ions increases down the group, opposite to the trend for the elements: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, because decreasing electronegativity and increasing ionic radius down the group give lower charge density and a greater ease of donating an electron. Fluoride's high electronegativity, strong hold on its extra electron, and small size (high charge density) make it the weakest reducing agent; chloride is a stronger reducing agent than fluoride due to its larger size and lower electronegativity; bromide is stronger still, with a larger ionic radius and lower charge density than chloride; and iodide, with the lowest electronegativity and largest size among the four, is the strongest reducing agent, most easily donating an electron.

13.8 Reactions of Halides with Aqueous Silver Ion and Ammonia

Halide ions react with aqueous silver nitrate to form insoluble silver halides ($\text{X}^- + \text{Ag}^+ \rightarrow \text{AgX}$), a reaction used in qualitative analysis: F^- gives no visible precipitate (AgF is soluble), Cl^- gives a white precipitate (AgCl), Br^- gives a cream-coloured precipitate (AgBr), and I^- gives a yellow precipitate (AgI). Adding aqueous ammonia afterward distinguishes the halides further by testing precipitate solubility: AgF (already soluble, unaffected by ammonia), AgCl dissolves in dilute ammonia to form the colourless diamminesilver(I) complex



($[\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$), AgBr dissolves only in concentrated ammonia, and AgI remains completely insoluble in ammonia (dilute or concentrated) -- together these two steps form the standard silver nitrate test for identifying halide ions.

13.9 Reactions of Halide Ions with Concentrated Sulfuric Acid

The reaction of halide ions with concentrated sulfuric acid changes character down the group as the reducing power of the halide ion increases. Fluoride and chloride, both weak reducing agents, simply produce their hydrogen halide gas by an acid-base (non-redox) reaction (e.g., $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$); bromide, a stronger reducing agent, additionally undergoes a redox side reaction in which HBr reduces H_2SO_4 to SO_2 and is itself oxidized to Br_2 ($2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O}$), producing HBr fumes, brown Br_2 fumes, and the smell of SO_2 ; and iodide, the strongest reducing agent, reduces H_2SO_4 all the way to H_2S while being oxidized to I_2 ($8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$), producing HI fumes, purple I_2 fumes, and the smell of H_2S .

13.10 Disproportionation of Chlorine with Sodium Hydroxide

A disproportionation reaction is one in which a single element is simultaneously oxidized and reduced. With cold aqueous NaOH, chlorine disproportionates to sodium chloride and sodium chlorate(I) ($\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$), with chlorine's oxidation state changing from 0 in Cl_2 to -1 in NaCl (reduction) and to +1 in NaClO (oxidation) simultaneously. With hot aqueous NaOH, chlorine instead disproportionates to sodium chloride and sodium chlorate(V) ($3\text{Cl}_2 + 6\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$), with chlorine going from 0 to -1 in NaCl (reduction) and to +5 in NaClO_3 (oxidation); this shows how reaction temperature controls which disproportionation products chlorine forms.

13.11 Use of Chlorine in Water Purification

Chlorine is widely used to disinfect drinking water and swimming pool water because, while poisonous in large amounts, small quantities are harmless to humans but lethal to disease-causing bacteria. When chlorine gas is added to water it hydrolyzes to form a mixture of hydrochloric acid and chloric(I) acid (hypochlorous acid), $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$; HClO is a weak acid that partially



dissociates to H^+ and chlorate(I) (hypochlorite) ion, OCl^- , and both HOCl and OCl^- are the primary active disinfecting species.

HOCl is the more effective disinfectant of the two because its neutral charge lets it penetrate microorganism cell walls more easily; both HOCl and OCl^- oxidize essential cellular proteins, lipids, enzymes, and nucleic acids, disrupting cell function, preventing bacterial replication, and ultimately causing cell death. Disinfection effectiveness depends on pH (HOCl predominates and is more effective around pH 6-7.5, while less-effective OCl^- predominates above pH 7.5), chlorine dose (more chlorine gives more active disinfecting species), and contact time (long enough for the disinfectant to penetrate and kill bacteria, viruses, and protozoa); chlorination remains a relatively inexpensive method of water disinfection.

Important Definitions

Why does fluorine's bond enthalpy (F-F) not follow the expected trend for the group?

Fluorine atoms are so small that the lone pairs on each bonded fluorine atom experience significant electron-electron repulsion, which weakens the F-F bond despite fluorine's high electronegativity, making F_2 's bond energy (156 kJ/mol) anomalously lower than Cl_2 's (243 kJ/mol).

What is the order of decreasing oxidizing power of the halogens?

$\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$, reflecting each halogen's decreasing tendency to gain an electron and form its halide ion as the group is descended.

What is the order of increasing reducing power of the halide ions?

$\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$, the opposite trend to the elements, because decreasing electronegativity and increasing ionic radius down the group make it progressively easier for the halide ion to donate an electron.

What are the colours of the silver halide precipitates?

AgCl is white, AgBr is cream-coloured, and AgI is yellow; AgF does not precipitate because it is soluble in water.

What is a disproportionation reaction?



A reaction in which a single element is simultaneously oxidized and reduced, forming two different products with different oxidation states.

What are the primary active disinfecting species when chlorine is added to water?

Chloric(I) acid (hypochlorous acid, HOCl) and the chlorate(I) (hypochlorite) ion, OCl⁻, both formed when chlorine hydrolyzes in water.

Why is HOCl a more effective disinfectant than OCl⁻?

HOCl carries no charge, which allows it to penetrate the cell walls of microorganisms more easily than the negatively charged OCl⁻ ion, making it more effective at reaching and oxidizing essential cellular components.

What is instantaneous dipole-induced dipole (id-id) force?

A weak, temporary intermolecular attractive force (a form of London dispersion force) arising from momentary fluctuations in electron distribution that induce a corresponding dipole in a neighbouring molecule; its strength increases with molecular size and polarizability.

Why does thermal stability of hydrogen halides decrease from HF to HI?

Thermal stability tracks bond dissociation energy directly; as atomic radius increases down the group from fluorine to iodine, orbital overlap between hydrogen and the halogen weakens, giving progressively lower bond dissociation energies and therefore progressively lower thermal stability.

Why is fluoride ion (F⁻) such a weak reducing agent compared to the other halide ions?

Fluorine's very high electronegativity and fluoride's small ionic size give it a strong hold on its extra electron and a high charge density, both of which make it very difficult for fluoride to donate an electron, so it acts as only a very weak reducing agent.

Key Facts and Relations

Topic	Key Fact / Relation
Order of oxidizing power (halogens)	F ₂ > Cl ₂ > Br ₂ > I ₂

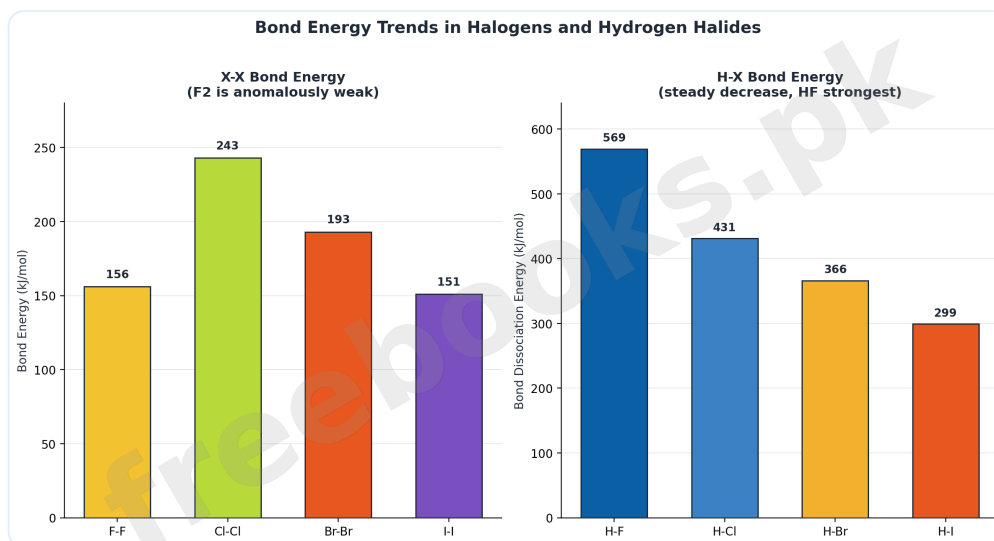


Topic	Key Fact / Relation
Order of reducing power (halide ions)	$I^- > Br^- > Cl^- > F^-$
Order of thermal stability (hydrogen halides)	$HF > HCl > HBr > HI$
X-X bond energies	$F_2 = 156, Cl_2 = 243, Br_2 = 193, I_2 = 151$ kJ/mol
H-X bond dissociation energies	$H-F = 569, H-Cl = 431, H-Br = 366, H-I = 299$ kJ/mol
Standard reduction potential $E(X_2/X^-)$	$F_2 = +2.87$ V, $Cl_2 = +1.36$ V, $Br_2 = +1.07$ V, $I_2 = +0.54$ V
Silver halide precipitate colours	AgF soluble (no ppt), AgCl white, AgBr cream, AgI yellow
Cold NaOH + Cl_2 (disproportionation)	$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$ (Cl: 0 $\rightarrow$ -1 and 0 $\rightarrow$ +1)
Hot NaOH + Cl_2 (disproportionation)	$3Cl_2 + 6NaOH \rightarrow NaCl + NaClO_3 + 3H_2O$ (Cl: 0 $\rightarrow$ -1 and 0 $\rightarrow$ +5)
Chlorine hydrolysis in water	$Cl_2 + H_2O \rightarrow HCl + HClO$ (active disinfectants: HOCl and OCl ⁻)

Diagrams

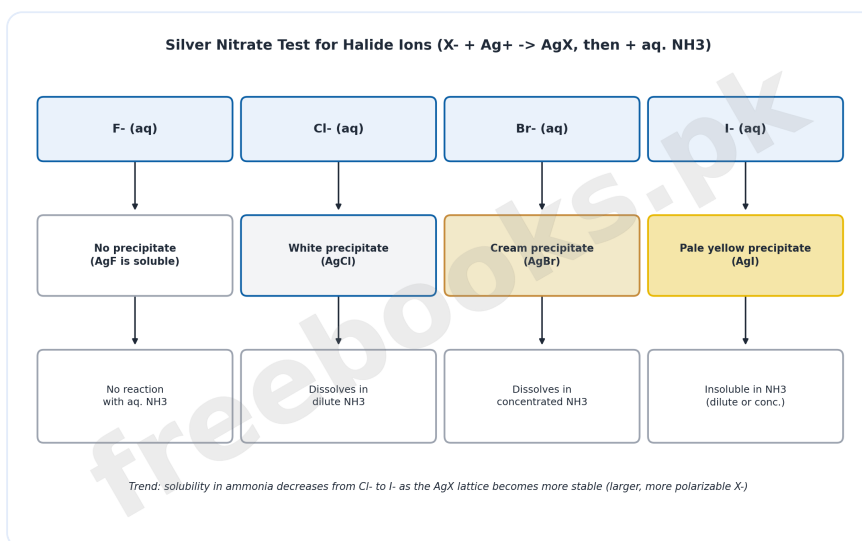
Bond Energy Trends in Halogens and Hydrogen Halides: Two side-by-side bar charts comparing X-X bond energies (showing fluorine's anomalous weakness) and H-X bond dissociation energies (showing a steady decrease from HF to HI) across the halogen group





Bond Energy Trends in Halogens and Hydrogen Halides

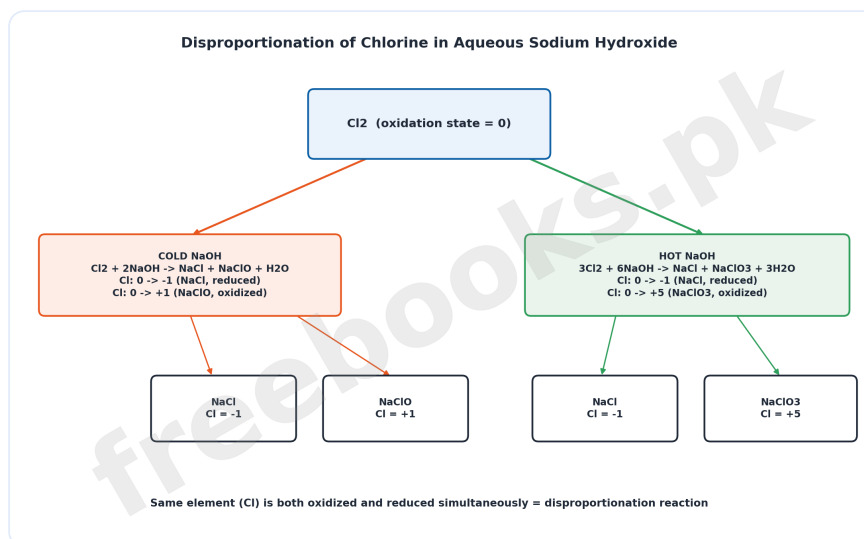
Silver Nitrate Test for Halide Ions: A flow diagram showing the silver halide precipitate colour and subsequent ammonia solubility for each halide ion, the standard qualitative test used to identify F⁻, Cl⁻, Br⁻, and I⁻



Silver Nitrate Test for Halide Ions

Disproportionation of Chlorine in Aqueous Sodium Hydroxide: A flow diagram comparing the cold and hot NaOH reactions of chlorine, tracking the oxidation state of chlorine in each product to show the simultaneous oxidation and reduction that defines disproportionation





Disproportionation of Chlorine in Aqueous Sodium Hydroxide

Short Questions & Answers

Why does volatility decrease from chlorine to iodine down the halogen group?

As the halogen group is descended, molecular mass and the size of the outer electron shell both increase, which strengthens the instantaneous dipole-induced dipole (London dispersion) forces between molecules; because stronger intermolecular forces require more energy to separate molecules from the liquid or solid phase into the gas phase, volatility decreases steadily from chlorine through bromine to iodine.

Why is the F-F bond weaker than the Cl-Cl bond, even though fluorine is the most electronegative element?

Bond strength here depends on more than electronegativity; because fluorine atoms are extremely small, the non-bonding lone pairs on each of the two bonded fluorine atoms are forced very close together, creating strong electron-electron repulsion that destabilizes and weakens the F-F bond, an effect that outweighs fluorine's high electronegativity and makes F₂'s bond energy anomalously low compared to Cl₂.

Why does the oxidizing power of the halogens decrease down the group from fluorine to iodine?

Oxidizing power reflects a halogen's ability to gain an electron and be reduced to its halide ion; as the group is descended, atomic size increases and the added electron is captured at a greater distance from the nucleus with more electron



shielding, reducing the halogen's overall attraction for that extra electron, so its tendency to be reduced (and therefore its oxidizing power) decreases from fluorine to iodine.

Why does fluorine react explosively with hydrogen even in the cold and dark, while iodine reacts with hydrogen only slowly, reversibly, and with a catalyst?

Fluorine has by far the highest oxidizing power and reactivity among the halogens, and its very weak F-F bond, along with the exceptionally strong H-F bond that forms, makes the reaction with hydrogen highly exothermic and kinetically very fast even without additional activation energy; iodine, by contrast, has the lowest oxidizing power, its I-I bond is comparatively easy to break but the resulting H-I bond is weak, so the reaction proceeds only slowly and reversibly, and needs a catalyst and high temperature to achieve a useful rate.

Why does thermal stability of the hydrogen halides decrease from HF to HI?

Thermal stability of a hydrogen halide is directly determined by the strength of its H-X bond, measured by bond dissociation energy; because atomic radius increases steadily from fluorine to iodine, the overlap between hydrogen's orbital and the halogen's orbital becomes progressively poorer down the group, giving progressively weaker H-X bonds and therefore progressively lower thermal stability, from the strongly bonded and highly stable HF down to the weakly bonded and least stable HI.

Why is iodide ion (I-) the strongest reducing agent among the halide ions?

Iodine has the lowest electronegativity of the common halogens and the iodide ion has the largest ionic radius, giving it the lowest charge density among the halide ions; this low charge density means the extra electron on iodide is held only loosely, making it comparatively easy for iodide to donate that electron to another species, which is exactly what makes it the strongest reducing agent in the group.

Why does silver iodide (AgI) remain insoluble in both dilute and concentrated aqueous ammonia, while silver chloride (AgCl) dissolves even in dilute ammonia?



The solubility of a silver halide in ammonia depends on how strongly the silver and halide ions are held together in the solid lattice compared to how strongly ammonia can compete for the silver ion by forming the diamminesilver(I) complex; AgI has the most stable (least soluble) ionic lattice among the silver halides because iodide's large size and high polarizability favour strong covalent-like interactions with silver, so even concentrated ammonia cannot compete effectively enough to dissolve it, unlike the more ionic and more soluble AgCl lattice.

Why does hydrogen iodide (HI) reduce concentrated sulfuric acid all the way to hydrogen sulfide (H₂S), while hydrogen chloride (HCl) does not reduce sulfuric acid at all?

Iodide is a much stronger reducing agent than chloride because of its larger size, lower electronegativity, and lower charge density, giving it a far greater tendency to donate electrons; this greater reducing strength allows HI to reduce sulfur in H₂SO₄ all the way down from the +6 oxidation state to the -2 oxidation state in H₂S, whereas HCl, formed from the much weaker reducing agent chloride, lacks the reducing power to reduce sulfuric acid at all and is simply released as HCl gas.

Why are the reactions of chlorine with cold and hot sodium hydroxide both classified as disproportionation reactions?

In both reactions, chlorine atoms starting at oxidation state 0 in Cl₂ end up in two different products with two different oxidation states simultaneously: in the cold reaction, chlorine is reduced to -1 in NaCl and oxidized to +1 in NaClO at the same time, while in the hot reaction, chlorine is reduced to -1 in NaCl and oxidized to +5 in NaClO₃ at the same time; because the same starting element is simultaneously oxidized and reduced in each case, both reactions fit the definition of disproportionation.

Why is HOCl considered a more effective disinfectant than OCl⁻ for killing bacteria in water?

HOCl is a neutral, uncharged molecule, which allows it to pass through the cell walls of bacteria far more easily than the negatively charged OCl⁻ ion, which is repelled or blocked more readily by the cell wall; because HOCl can penetrate into the cell interior more effectively, it has greater direct access to oxidize the



proteins, lipids, enzymes, and nucleic acids essential to bacterial survival, making it the more potent of the two disinfecting species.

Long Questions & Answers

Explain the trend in oxidizing power of the halogens and the trend in reducing power of the halide ions, and describe how the silver nitrate test and concentrated sulfuric acid reactions can be used to distinguish between the halide ions.

Why does the oxidizing power of the halogens decrease down the group from fluorine to iodine?

Oxidizing power measures how readily a halogen gains an electron to form its halide ion; as atomic size increases down the group, the incoming electron experiences greater shielding and is added at a greater average distance from the nucleus, weakening the halogen's overall pull on that electron, so the tendency to be reduced, and therefore the oxidizing power, decreases steadily from fluorine to iodine.

Why is the trend in reducing power of the halide ions the exact opposite of the trend in oxidizing power of the halogens?

Reducing power measures a halide ion's willingness to lose (donate) an electron, the reverse process of oxidizing power; because ionic radius increases and electronegativity decreases down the group, charge density on the halide ion falls steadily from fluoride to iodide, making it progressively easier for the ion to release its extra electron, so the reducing power of the halide ions increases in the opposite direction ($I^- > Br^- > Cl^- > F^-$) to the oxidizing power of the corresponding elements.

How does the silver nitrate test distinguish between the four halide ions?

Adding aqueous silver nitrate to each halide solution produces a precipitate with a distinctive appearance: no visible precipitate for fluoride (AgF is soluble), a white precipitate for chloride ($AgCl$), a cream-coloured precipitate for bromide



(AgBr), and a yellow precipitate for iodide (AgI); these differing precipitate colours alone can distinguish most of the halide ions from each other.

How does testing the precipitate's solubility in aqueous ammonia add further confirmation?

Following up with aqueous ammonia distinguishes the halides even more precisely by testing how easily each silver halide's ionic lattice can be broken apart by ammonia forming a diamminesilver(I) complex: AgCl dissolves in dilute ammonia, AgBr requires concentrated ammonia to dissolve, and AgI remains completely insoluble in ammonia at any concentration, giving three distinct, unambiguous outcomes.

How does the reaction with concentrated sulfuric acid provide an independent way to distinguish bromide and iodide in particular?

Because bromide and iodide are stronger reducing agents than fluoride and chloride, they trigger visibly different redox side reactions with concentrated sulfuric acid: sodium bromide produces HBr fumes together with brown Br₂ fumes and the smell of SO₂ (as HBr reduces H₂SO₄ to SO₂), while sodium iodide produces HI fumes together with purple I₂ fumes and the smell of H₂S (as HI reduces H₂SO₄ all the way to H₂S); these distinct, easily observable colours and smells allow bromide and iodide to be confidently distinguished from each other and from the non-redox fluoride and chloride reactions.

Explain how chlorine's reactions with sodium hydroxide demonstrate disproportionation, and describe how chlorine's chemistry in water underlies its use as a water disinfectant.

What happens to chlorine's oxidation state when it reacts with cold, dilute aqueous sodium hydroxide?

In the reaction $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$, chlorine starts at oxidation state 0 in Cl₂ and splits into two different products: one chlorine atom is reduced to oxidation state -1 in NaCl, while the other chlorine atom is oxidized to oxidation state +1 in NaClO, meaning the same starting element is simultaneously reduced and oxidized in a single reaction.



How does the reaction change when hot, concentrated aqueous sodium hydroxide is used instead, and why does this still count as disproportionation?

With hot NaOH, the reaction becomes $3\text{Cl}_2 + 6\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$, and chlorine again splits into two oxidation states from the same starting point of 0: one portion is reduced to -1 in NaCl, while the other portion is oxidized much further, all the way to +5 in NaClO₃; because chlorine is still being simultaneously oxidized and reduced from a single starting oxidation state, this reaction is disproportionation as well, just with a more oxidized product favoured at higher temperature.

What happens chemically when chlorine gas is added to water, and what two active species does this produce?

Chlorine gas hydrolyzes in water via $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}$, producing hydrochloric acid and chloric(I) acid (hypochlorous acid); the weak acid HClO then partially dissociates further into H⁺ and chlorate(I) (hypochlorite) ion, OCl⁻, so the two species responsible for chlorine's disinfecting action in water are HOCl and OCl⁻.

Why is HOCl generally considered the more effective of these two disinfecting species?

HOCl is electrically neutral, which allows it to pass through the cell walls of bacteria and other microorganisms much more readily than the negatively charged OCl⁻ ion; once inside the cell, HOCl can directly oxidize essential proteins, lipids, enzymes, and nucleic acids, disrupting vital cellular functions and preventing replication, giving it stronger overall disinfecting power than OCl⁻ despite both species being active.

What practical factors determine how effective chlorination is at disinfecting a water supply?

Effectiveness depends on pH (HOCl predominates and disinfection is most effective around pH 6-7.5, while the less effective OCl⁻ predominates above pH 7.5), the dose of chlorine added (more chlorine produces more of the active disinfecting species), and contact time (water must remain in contact with the



chlorine disinfectants long enough for them to penetrate and kill bacteria, viruses, and protozoa); all three factors must be adequately controlled for chlorination to reliably disinfect a water supply.

Multiple Choice Questions (MCQs)

Which halogen molecule has the strongest X-X bond?

- A. F₂
- B. Cl₂
- C. Br₂
- D. I₂

Answer: B. Cl₂

Explanation: Cl₂ has the strongest halogen-halogen bond (243 kJ/mol); F₂'s bond is anomalously weak (156 kJ/mol) due to lone-pair repulsion between the small fluorine atoms, making Cl₂, not F₂, the strongest in the group.

What happens to the volatility of the halogens as you move down the group from fluorine to iodine?

- A. It increases steadily
- B. It decreases steadily
- C. It remains constant
- D. It fluctuates with no clear trend

Answer: B. It decreases steadily

Explanation: Volatility decreases down the group as increasing molecular size and polarizability strengthen instantaneous dipole-induced dipole (London dispersion) forces, requiring more energy to vaporize the larger halogens.

Which halogen has the strongest oxidizing power?

- A. Br₂
- B. F₂
- C. I₂
- D. Cl₂

Answer: B. F₂

Explanation: Fluorine (F₂) has the strongest oxidizing power among the halogens, decreasing down the group in the order F₂ > Cl₂ > Br₂ > I₂.



What is the main reason the thermal stability of hydrogen halides decreases down the group from HF to HI?

- A. Increasing electronegativity of the halogen
- B. Decreasing bond length between H and X
- C. Increasing atomic radius of the halogen, leading to weaker H-X bond overlap
- D. Increasing strength of van der Waals forces between HX molecules

Answer: C. Increasing atomic radius of the halogen, leading to weaker H-X bond overlap

Explanation: As atomic radius increases from fluorine to iodine, orbital overlap between hydrogen and the halogen becomes progressively poorer, weakening the H-X bond and reducing thermal stability, giving the order $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$.

Which halide ion is the strongest reducing agent?

- A. F^-
- B. Cl^-
- C. Br^-
- D. I^-

Answer: D. I^-

Explanation: Iodide (I^-) is the strongest reducing agent among the halide ions because its low electronegativity and large ionic radius give it the lowest charge density, making it easiest to donate an electron.

A cream-coloured precipitate forms when aqueous silver nitrate is added to a solution. What is this precipitate's solubility in aqueous ammonia?

- A. Soluble in dilute ammonia
- B. Insoluble in both dilute and concentrated ammonia
- C. Soluble only in concentrated ammonia
- D. Soluble upon heating with dilute ammonia only

Answer: C. Soluble only in concentrated ammonia

Explanation: A cream-coloured precipitate indicates silver bromide (AgBr), which is only soluble in concentrated aqueous ammonia, not dilute ammonia.

What is observed when concentrated sulfuric acid is added to solid sodium chloride?



- A. Reddish-brown fumes are evolved
- B. Purple vapour is evolved
- C. Steamy white fumes of hydrogen chloride are evolved
- D. A black solid is formed

Answer: C. Steamy white fumes of hydrogen chloride are evolved

Explanation: $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$ is a simple non-redox reaction, producing steamy white fumes of hydrogen chloride gas, with no colour change since chloride is too weak a reducing agent to reduce sulfuric acid further.

In the reaction $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaCl} + \text{NaClO} + \text{H}_2\text{O}$, what are the oxidation states of chlorine in the two products?

- A. -1 in NaCl and +1 in NaClO
- B. 0 in NaCl and +1 in NaClO
- C. -1 in NaCl and -1 in NaClO
- D. +1 in NaCl and -1 in NaClO

Answer: A. -1 in NaCl and +1 in NaClO

Explanation: Chlorine starts at oxidation state 0 in Cl_2 and is simultaneously reduced to -1 in NaCl and oxidized to +1 in NaClO, making this a disproportionation reaction.

Which species is considered the more effective disinfectant in chlorinated water, and why?

- A. OCl^- , because it is negatively charged and attracts bacteria
- B. HOCl, because its neutral charge allows it to penetrate microbial cell walls more easily
- C. Cl_2 gas itself, because it does not need to dissolve in water
- D. NaCl, because it is the most abundant chlorine species in solution

Answer: B. HOCl, because its neutral charge allows it to penetrate microbial cell walls more easily

Explanation: HOCl is the more effective disinfectant because its neutral charge allows it to penetrate bacterial cell walls more easily than the negatively charged OCl^- ion, giving it greater access to oxidize essential cellular components.

Which reaction with concentrated sulfuric acid indicates the strongest reducing power among the halide ions tested?

- A. $\text{NaF} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HF}$
- B. $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$





Answer: D. $8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$

Explanation: Iodide's reaction reduces sulfur all the way from +6 in H_2SO_4 to -2 in H_2S , a far greater degree of reduction than bromide achieves (reducing sulfur only to +4 in SO_2), demonstrating iodide's superior reducing power.

Quick Revision Summary

- Halogens = group 17: F, Cl, Br, I (common), At, Ts (rare, radioactive); exist as diatomic X_2 molecules, colours darken $\text{F} < \text{Cl} < \text{Br} < \text{I}$
- Volatility decreases down group ($\text{Cl} > \text{Br} > \text{I}$) due to increasing molecular size/mass strengthening London dispersion (id-id) forces
- X-X bond energy: Cl_2 (243) > Br_2 (193) > F_2 (156) > I_2 (151) -- F_2 anomalously weak due to lone-pair repulsion (small atoms)
- Oxidizing power of halogens: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$; each can displace halide ions below it from solution
- Reactivity with H_2 : F_2 (explosive, cold/dark) > Cl_2 (UV/spark) > Br_2 (heat) > I_2 (catalyst, slow, reversible)
- Thermal stability of HX : $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$, tracks H-X bond dissociation energy (569, 431, 366, 299 kJ/mol)
- Reducing power of halide ions (opposite trend): $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$, due to decreasing electronegativity/increasing size down group
- AgNO_3 test: AgF soluble (no ppt), AgCl white (soluble dil. NH_3), AgBr cream (soluble conc. NH_3), AgI yellow (insoluble in NH_3)
- Conc. H_2SO_4 + halide: F^-/Cl^- give simple HX fumes (no redox); Br^- gives $\text{HBr} + \text{Br}_2 + \text{SO}_2$ (redox); I^- gives $\text{HI} + \text{I}_2 + \text{H}_2\text{S}$ (stronger redox)
- Disproportionation: $\text{Cl}_2 + \text{cold NaOH} \rightarrow \text{NaCl} (-1) + \text{NaClO} (+1)$; $\text{Cl}_2 + \text{hot NaOH} \rightarrow \text{NaCl} (-1) + \text{NaClO}_3 (+5)$
- Chlorine in water: $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$; active disinfectants = HOCl and OCl^- ; HOCl more effective (neutral, penetrates cell walls)
- Disinfection factors: pH (HOCl favoured pH 6-7.5, OCl^- above 7.5), chlorine dose, contact time



Exam Tips

- Remember fluorine breaks the 'smooth trend' pattern twice: it has the strongest oxidizing power AND lowest X-X bond energy relative to chlorine -- don't assume bond strength and reactivity always move together
- Keep the oxidizing power trend ($F_2 > Cl_2 > Br_2 > I_2$) and reducing power trend ($I^- > Br^- > Cl^- > F^-$) straight -- they run in opposite directions because one is about the element gaining an electron and the other is about the ion losing one
- For $AgNO_3/NH_3$ test questions, memorize the precipitate colour AND its ammonia solubility together as a pair (e.g. 'cream = concentrated ammonia') rather than separately
- For concentrated H_2SO_4 + halide reactions, remember only Br^- and I^- trigger true redox side-reactions (extra fumes/smell); F^- and Cl^- just give simple HX gas with no redox
- For disproportionation questions, always write out the oxidation state of the element in every species (reactant and all products) before deciding which reaction is oxidation and which is reduction
- When explaining why chlorine is used for disinfection, mention both active species ($HOCl$ and OCl^-) and always state WHY $HOCl$ is more effective (neutral charge, easier cell penetration) rather than just naming it



Chapter 14: Atmosphere

The atmosphere is a sphere of gases surrounding the earth, made up of major components nitrogen (78.00%) and oxygen (21.01%), minor components argon (0.93%) and carbon dioxide (0.04%), and trace components such as methane, hydrogen, neon, helium, krypton, and xenon. It is organized into four distinct layers, defined by how temperature changes with altitude: the troposphere (0-12 km, where weather occurs and temperature falls steadily), the stratosphere (12-50 km, home to the protective ozone layer), the mesosphere (50-80 km, the coldest layer), and the thermosphere (80-600 km, where temperature rises sharply due to absorption of UV and X-rays).

Human and natural activity release a wide range of air pollutants into this system, including oxides of carbon, nitrogen, and sulfur, hydrocarbons, low-altitude ozone, chlorofluorocarbons (CFCs), polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), volatile organic compounds (VOCs), particulate matter, and heavy metals. These pollutants drive chemical processes such as smog formation, acid rain, stratospheric ozone depletion, and the greenhouse effect, each with measurable impacts on air quality (tracked via the Air Quality Index, AQI) and human health, and each addressed through specific pollution-control technologies, laws, and regulations.

Learning Objectives

- Identify the properties, composition, and four layers of the atmosphere
- Describe the sources and effects of natural and human-made air pollution
- Describe the impact of human activities, including burning fossil fuels and deforestation, on the atmosphere
- Identify chemical reactions and processes occurring in the atmosphere, including smog and acid rain formation
- Identify global-scale air pollution problems such as global warming and the greenhouse effect
- Describe the factors that affect air quality and explain the link between air quality and human health



- Evaluate the potential health risks associated with air pollution
- Familiarize with methods and techniques used to measure and monitor air quality
- Explain technologies and strategies used to reduce air pollution and improve air quality
- Identify laws, regulations, and the economic, social, and political issues related to air quality management

Key Concepts

14.1 Composition and Layers of the Atmosphere

The atmosphere's components divide into major components, nitrogen (78.00%) and oxygen (21.01%); minor components, argon (0.93%) and carbon dioxide (0.04%); and trace components, including methane, hydrogen, neon, helium, krypton, and xenon. The atmosphere has four distinct layers, determined by how temperature changes with increasing altitude.

The troposphere is the lowest, densest layer, extending up to 12 km and containing all the major atmospheric gases; temperature falls steadily from 17 degC to -58 degC, and it is the layer in which rain, lightning, and hurricanes occur. Above it, the stratosphere (12-50 km) sees temperature rise from -58 degC to -2 degC and hosts the ozone layer: in the upper stratosphere, ozone absorbs high-energy UV radiation and breaks down ($O_3 \xrightarrow{UV} O_2 + O$), while in the middle stratosphere, monatomic and diatomic oxygen recombine exothermically to reform ozone ($O_2 + O \rightarrow O_3$); the lower stratosphere receives very little UV, so little monatomic oxygen or ozone forms there.

The mesosphere (50-80 km) is the coldest layer, with temperature falling from -2 degC to -93 degC. The thermosphere (80-600 km) is where temperature rises sharply with altitude, from around 500 degC to 2000 degC or higher, due to absorption of energetic UV and X-ray radiation.

14.2 Air Pollutants and Their Sources

Pollutants are harmful substances (gases, liquids, or solids) classified as primary pollutants, directly emitted (e.g., volcanic ash, vehicle exhaust CO), or secondary



pollutants, formed from chemical reactions of primary pollutants. The most important pollutants are oxides of carbon (CO, CO₂), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), hydrocarbons, low-altitude ozone, CFCs, PAHs, POPs, VOCs, particulate matter (PM), and heavy metals (Pb, Hg, Cd).

Air pollution has two broad sources. Natural sources include windblown dust and biological debris, volcanic eruptions (releasing large quantities of gases and PM), thunderbolts (producing NO_x), ocean algae (releasing H₂S), and humid zones such as swamps and peat bogs (producing methane). Human-made sources are classified as mobile (cars, trucks, planes, marine engines) or point sources (factories, power plants); burning fossil fuels in vehicles, factories, and power plants produces CO₂, CO, and hydrocarbons, while burning wood domestically and coal in brick kilns add further pollutants.

14.3 Oxides of Carbon, Nitrogen, and Sulfur; Hydrocarbons; Low-Altitude Ozone

Carbon monoxide (CO) forms mainly from incomplete combustion of fossil fuels ($2C + O_2 \rightarrow 2CO$); it is highly poisonous, binding haemoglobin more strongly than oxygen and excluding oxygen from respiration, though CO poisoning can be reversed with high-pressure oxygen. Carbon dioxide (CO₂) forms from complete combustion ($C + O_2 \rightarrow CO_2$) and is the key greenhouse gas emitted by human activity, trapping heat and driving global warming.

Oxides of nitrogen (NO_x = NO and NO₂) form from $N_2 + O_2 \xrightarrow{\text{high T}} 2NO$, followed by $2NO + O_2 \rightarrow 2NO_2$; natural sources include soil and ocean microbial processes, while human sources include synthetic fertilizers and fossil fuel combustion. NO_x depletes the ozone layer and contributes to climate change and reduced air quality. Oxides of sulfur (SO_x = SO₂, SO₃) are emitted mainly by burning coal and oil; when they combine with water vapour they cause acid rain, with SO₂ the major source of acid deposition.

Hydrocarbons arise naturally (vegetation, wildfires, volcanoes, seeps) and anthropogenically (incomplete fossil fuel combustion, oil spills, industrial and vehicular emissions), with automobiles the major source and methane the most common hydrocarbon pollutant. Low-altitude ozone (O₃) is a powerful oxidizing



agent, non-toxic at small concentrations but toxic above 100 ppm, harming humans, plants, rubber, and fabric dyes.

14.4 CFCs, PAHs, POPs, VOCs, Particulate Matter, and Heavy Metals

Chlorofluorocarbons (CFCs), used as aerosol propellants and refrigerants, diffuse into the stratosphere where UV radiation breaks them down into chlorine free radicals that destroy ozone in a catalytic chain: $\text{CFCl}_3 \xrightarrow{\text{UV}} \text{CFCl}_2 + \text{Cl} \cdot$; $\text{Cl} \cdot + \text{O}_3 \rightarrow \text{ClO} \cdot + \text{O}_2$; $\text{ClO} \cdot + \text{O} \rightarrow \text{Cl} \cdot + \text{O}_2$, regenerating the chlorine radical so it can destroy further O_3 molecules. One CFC molecule can destroy up to 100,000 ozone molecules, and CFCs are about 100,000 times more effective than CO_2 at trapping heat.

Polycyclic aromatic hydrocarbons (PAHs; e.g., naphthalene, anthracene, phenanthrene) form from incomplete combustion of fossil fuels and even grilled foods, and are toxic and carcinogenic. Persistent organic pollutants (POPs), such as PCBs (used in electrical equipment, coatings, adhesives) and DDT (an insecticide), resist chemical, biological, and photolytic degradation, travel long distances via wind and water, and accumulate in the environment.

Volatile organic compounds (VOCs) evaporate easily at room temperature from vehicle exhaust and burning liquid fuels, wood, and garbage; short-term exposure causes eye, nose, and throat irritation, headache, and nausea, while long-term exposure damages the liver, kidney, and nervous system (common VOCs: benzene, xylene, toluene, ethanol, formaldehyde, acetone). Particulate matter (PM) is tiny suspended solid or liquid particles from both natural sources (volcanoes, fires, dust storms, sea salt) and human sources (combustion, vehicle emissions, tobacco smoke). Heavy metals (lead, mercury, cadmium) enter the air mainly from metallurgy, battery waste, and incineration.

14.5 Impact of Human Activities on the Atmosphere

Human activities affect the atmosphere primarily through burning fossil fuels and deforestation, driving climate change, air pollution, and poor air quality; in urban areas, most pollution comes from human-made mobile and point sources.

Burning fossil fuels is the primary cause of current climate change, releasing greenhouse gases, air pollutants, and VOCs that alter the earth system and harm human health.



Deforestation, the purposeful clearing or thinning of forests, removes trees that would otherwise absorb greenhouse gases like CO₂ and clean the air; it is one of the largest contributors to global climate change and causes loss of biodiversity, soil degradation, and disruption of the water cycle in addition to its direct effect on atmospheric CO₂ levels.

14.6 Formation of Smog and Acid Rain

Smog is thick, hazy air pollution common in urban areas, containing fine dust or soot, condensed water vapour, poisonous gases (SO₂, NO_x, O₃, CO, CO₂), and secondary pollutants (O₃, unburned hydrocarbons, VOCs, PM of 2.5-10 microns). Industrial or classical smog (London smog) results from high quantities of sulfur oxides being released into the air. Photochemical smog (Los Angeles smog) forms when primary pollutants like NO_x, VOCs, and unburned hydrocarbons undergo photochemical reactions in sunlight, producing secondary pollutants like ozone and peroxyacetyl nitrates (PAN); it is considered more dangerous, able to cause heart palpitations, pneumonia, and even lung cancer.

Acid rain is precipitation with pH below 5.6. Burning fossil fuels releases SO_x and NO_x, which mix with atmospheric moisture to form acids that wind can carry long distances before they fall as acid rain, hail, snow, or fog. Key reactions: $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$, then $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ (sulfuric acid); and $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, then $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$ (nitric acid). Acid rain looks, feels, and tastes like clean rain but is highly corrosive to the environment.

14.7 Greenhouse Effect and Global Warming

Global warming is the long-term rise in Earth's average surface temperature, driven mainly by human emission of greenhouse gases (GHGs) from burning fossil fuels. The greenhouse effect is the progressive warming of the earth's surface caused by the blanketing effect of these gases in the atmosphere. CO₂ and water vapour transmit short-wavelength solar radiation but reflect back the longer-wavelength heat radiation from the warmed earth's surface.

By day, infrared heat from the sun passes through the atmosphere and warms the earth; at night, the earth radiates heat back to space, but greenhouse gases trap some of this heat, preventing its full loss. The higher the concentration of



CO₂ and other greenhouse gases, the greater the absorption of thermal radiation and the greater the rise in global temperature.

14.8 Air Quality, the AQI, and Human Health

Air quality is measured using the Air Quality Index (AQI), which reflects pollutant concentrations at a location; good air quality is clear with few solid particles or chemical pollutants, while poor air quality is hazy and dangerous. An AQI under 50 is considered good and safe for outdoor activity; an AQI over 300 is hazardous. Children under 18, adults over 65, people with chronic heart or lung disease, and outdoor workers with prolonged exposure face the highest risk.

Air quality is influenced by emission sources (wood/fossil fuel burning, factories, vehicles releasing SO_x, NO_x, CO, PM, VOCs), meteorological conditions (wind, temperature, and humidity affect pollutant dispersion; warm air layers can trap pollutants near the ground), natural events (wildfires, dust storms), and seasonal changes (heating/cooling emissions, seasonal pollen). The AQI scale runs: 0-50 Good (green), 51-100 Moderate (yellow), 101-150 Unhealthy for Sensitive Groups (orange), 151-200 Unhealthy (red), 201-300 Very Unhealthy (purple), 301-500 Hazardous (maroon).

Poor air quality has immediate and long-term health impacts. Particulate matter (PM, 2.5-10 micrometers in diameter) causes airway inflammation and irritation, leading to asthma and bronchitis. Short-term exposure to NO₂ and SO₂ irritates the respiratory system; long-term exposure raises the risk of respiratory infection, asthma, and bronchitis. Broader health risks include respiratory diseases (triggered by ozone, PM, NO₂), cardiovascular disease (inflammation, blood vessel damage, high blood pressure, heart attack or stroke), cancer (especially from PM and carcinogens like benzene), and reproductive/developmental effects (reduced fertility, premature birth, developmental problems).

14.9 Measuring, Monitoring, and Analyzing Air Quality

Measuring and monitoring air quality tracks concentrations of PM, NO₂, SO₂, CO, O₃, and VOCs. The nephelometer (also called a photometer) is used to monitor PM such as dust, smoke, mist, and fumes by measuring the light they scatter. Direct measurement methods include continuous emission monitoring systems



(CEMS) at industrial sites, fixed air quality monitoring stations (AQMS) with real-time sensors in urban and industrial areas, and remote sensing via satellites for regional and global data.

Testing hypotheses about air quality follows a scientific process: forming a hypothesis (e.g., that PM_{2.5} and NO₂ are higher during peak traffic hours), designing the experiment (choosing sites such as busy roads and residential areas, planning variables and data-collection methods), collecting data (comparing rush-hour versus non-rush-hour measurements with reliable instruments), and finally analyzing and interpreting the data to confirm or reject the hypothesis and identify trends over time, informing strategies to improve air quality.

14.10 Strategies, Laws, and Economic, Social, and Political Issues

Technologies to reduce vehicle and industrial emissions include the catalytic converter (oxidizes CO to CO₂, reduces NO_x to N₂, converts unburnt hydrocarbons to CO₂ and H₂O), the diesel particulate filter (DPF, captures and stores soot particles from diesel exhaust), selective catalytic reduction (SCR, reduces NO_x to N₂ and oxidizes CO and hydrocarbons using catalysts like TiO₂ or zeolites), and scrubbers (use liquids such as water to remove PM, SO₂, HCl, NH₃, and VOCs).

Pakistan's air quality laws and regulations include the Pakistan Environmental Protection Act (PEPA 1997), the National Environmental Quality Standards (NEQS), and the Punjab Environmental Protection (Amendment) Act 2012. Control measures include vehicle emission standards and cleaner fuels (CNG, LPG), industrial emission control and cleaner production techniques, public awareness campaigns (public transport, carpooling, cycling, walking), urban planning and green infrastructure, smog control measures (restricting crop-residue burning, smog towers), and prohibiting open burning of waste.

Air pollution carries economic costs (reduced worker productivity, damaged crops and lower agricultural yield, higher food prices, acid rain damage), social costs (disproportionate impact on children, the elderly, and low-income communities; reduced quality of life; forced migration and social displacement), and political



challenges (pollution crosses borders, requiring international cooperation and strict governance to balance socio-economic and technological considerations).

Important Definitions

What determines the boundaries of the atmosphere's four layers?

The change in temperature observed with increasing altitude; each layer (troposphere, stratosphere, mesosphere, thermosphere) is defined by a distinct temperature trend as altitude increases.

What is the difference between primary and secondary air pollutants?

Primary pollutants are substances directly emitted into the air, such as volcanic ash or vehicle exhaust CO, while secondary pollutants form from chemical reactions of primary pollutants, such as ozone and PAN in photochemical smog.

What is depletion of ozone, and what causes it?

Depletion of ozone is the decrease in ozone concentration in the stratosphere, caused mainly by chlorofluorocarbons (CFCs), which diffuse into the stratosphere and are broken down by UV radiation into chlorine free radicals that destroy ozone molecules.

What are persistent organic pollutants (POPs)?

Organic compounds that resist degradation through chemical, biological, and photolytic processes, allowing them to travel via wind and water, accumulate in the environment, and adversely affect human health and wildlife far from where they were released.

What is smog, and what are its two main types?

Smog is a thick, hazy form of air pollution common in urban areas; its two main types are industrial or classical smog (London smog, caused by high sulfur oxide levels) and photochemical smog (Los Angeles smog, formed by sunlight-driven reactions of NO_x and VOCs).

What is acid rain?

Precipitation (rain, snow, hail, or fog) with a pH below 5.6, formed when SO_x and NO_x released from burning fossil fuels mix with atmospheric moisture to form sulfuric and nitric acids.

What is the greenhouse effect?



The progressive warming of the earth's surface caused by the blanketing effect of greenhouse gases in the atmosphere, which transmit incoming short-wavelength solar radiation but trap outgoing longer-wavelength heat radiation from the earth's surface.

What is the Air Quality Index (AQI)?

A measure of the concentration of pollutants present in the air at a particular location, used to communicate how clean or polluted the air is and what associated health effects might be a concern, on a scale from 0 (best) to 500 (worst).

What instrument is used to measure particulate matter in the air, and how does it work?

A nephelometer (also called a photometer) is used; it detects particles such as dust, smoke, mist, and fumes by measuring the total amount of light they scatter.

What is a catalytic converter, and what does it do?

A device fitted to most vehicle exhaust systems that converts harmful pollutants to harmless substances: it oxidizes CO to CO₂, reduces NO_x to N₂, and converts unburnt hydrocarbons to CO₂ and H₂O.

Key Facts and Relations

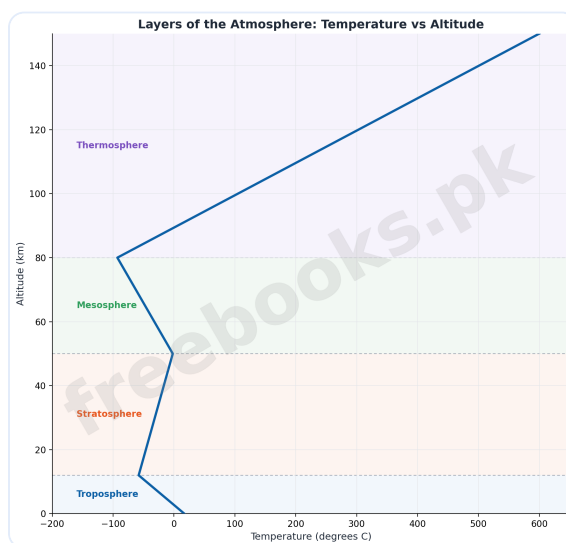
Topic	Key Fact / Relation
Major atmospheric components	N ₂ = 78.00%, O ₂ = 21.01% (minor: Ar 0.93%, CO ₂ 0.04%)
Atmospheric layers (altitude, temperature trend)	Troposphere 0-12 km (17 to -58 degC); Stratosphere 12-50 km (-58 to -2 degC); Mesosphere 50-80 km (-2 to -93 degC); Thermosphere 80-600 km (rises sharply)
Stratospheric ozone formation/depletion	O ₃ --UV--> O ₂ + O ; O ₂ + O -> O ₃ (exothermic)
CFC ozone-depletion chain	CFCI ₃ --UV--> CFCI ₂ + Cl. ; Cl. + O ₃ -> ClO. + O ₂ ; ClO. + O -> Cl. + O ₂



Topic	Key Fact / Relation
Acid rain formation (sulfuric acid)	$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$; $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$
Acid rain formation (nitric acid)	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$; $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$
Carbon oxide formation	$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ (incomplete combustion) ; $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ (complete combustion)
NO _x formation	$\text{N}_2 + \text{O}_2 \xrightarrow{\text{high T}} 2\text{NO}$; $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
AQI scale and health concern levels	0-50 Good; 51-100 Moderate; 101-150 Unhealthy for Sensitive Groups; 151-200 Unhealthy; 201-300 Very Unhealthy; 301-500 Hazardous
Acid rain threshold	Rainwater pH below 5.6 is classified as acid rain

Diagrams

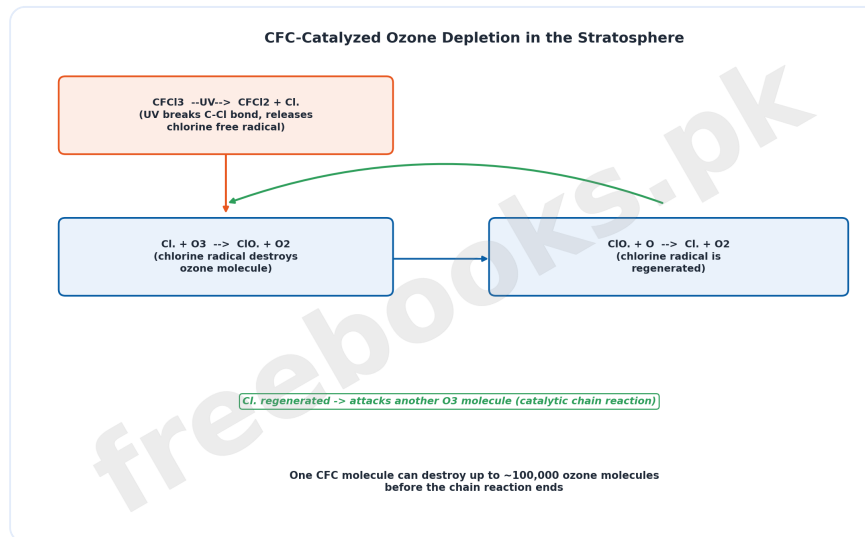
Layers of the Atmosphere: Temperature vs Altitude: A line plot showing how temperature changes with altitude across all four atmospheric layers -- troposphere, stratosphere, mesosphere, and thermosphere -- highlighting the alternating cooling and warming trends that define each layer's boundary



Layers of the Atmosphere: Temperature vs Altitude

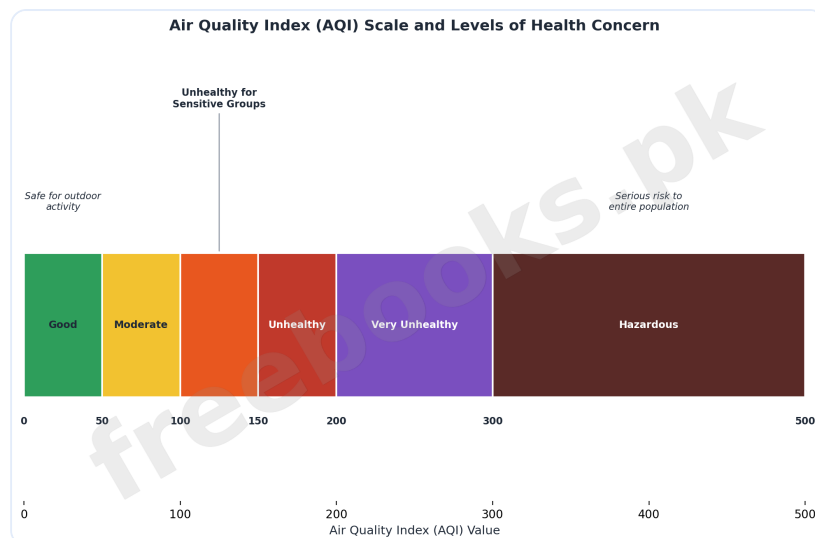


CFC-Catalyzed Ozone Depletion Mechanism: A flow diagram showing the three-step catalytic chain reaction by which a chlorine free radical from CFC photolysis destroys ozone and is continuously regenerated to destroy further ozone molecules



CFC-Catalyzed Ozone Depletion Mechanism

Air Quality Index (AQI) Scale and Levels of Health Concern: A colour-coded horizontal scale showing the six AQI bands from Good to Hazardous, their numeric ranges, and the associated level of health concern



Air Quality Index (AQI) Scale and Levels of Health Concern



Short Questions & Answers

Why does temperature decrease in the troposphere but increase in the stratosphere?

In the troposphere, the earth's surface absorbs solar radiation and re-radiates heat, so air closer to the ground is warmer, and temperature drops steadily as altitude (and distance from this heat source) increases; in the stratosphere, ozone in the upper layer directly absorbs high-energy ultraviolet radiation from the sun, releasing heat as it does so, which causes temperature to rise with altitude despite the layer being far from the earth's surface.

Why is carbon monoxide dangerous even though it is not directly explosive or corrosive?

Carbon monoxide binds to haemoglobin in the blood more strongly than oxygen does, so even a small concentration of CO in inhaled air can occupy a large share of the body's oxygen-carrying capacity; this excludes oxygen from normal respiration and causes suffocation at the cellular level, which is why CO poisoning is treated by administering high-pressure oxygen to help displace it from haemoglobin.

Why are CFCs considered catalysts in ozone depletion rather than simple reactants?

A true reactant is consumed in a reaction, but the chlorine free radical released by CFC photolysis is regenerated at the end of the ozone-destroying cycle ($\text{ClO} \cdot + \text{O} \rightarrow \text{Cl} \cdot + \text{O}_2$), meaning the same chlorine atom can go on to destroy many more ozone molecules; because it speeds up ozone destruction without being permanently consumed, it behaves as a catalyst, which is why a single CFC molecule can destroy up to 100,000 ozone molecules.

Why is photochemical smog considered more dangerous than industrial (classical) smog?

Industrial smog mainly involves sulfur oxides and is associated with cooler, damper climates, while photochemical smog forms when nitrogen oxides and VOCs react in strong sunlight to produce ozone and peroxyacetyl nitrates (PAN), both of which are aggressive respiratory irritants; because photochemical smog's secondary pollutants can trigger heart palpitations, pneumonia, and even lung



cancer, it is generally regarded as more harmful to human health than classical smog.

How do sulfur oxides and nitrogen oxides both lead to acid rain through similar chemical pathways?

Both pollutant families undergo a two-step oxidation-then-hydration pathway: SO₂ is oxidized to SO₃, which reacts with water to form sulfuric acid (H₂SO₄), while NO is oxidized to NO₂, which reacts with water to form nitric acid (HNO₃) alongside more NO; in both cases, the oxide combines with atmospheric moisture to form a strong acid that lowers rainwater pH below the 5.6 threshold that defines acid rain.

Why does an increase in atmospheric CO₂ concentration lead to an increase in global temperature?

CO₂ and water vapour let short-wavelength solar radiation pass through to warm the earth's surface, but they absorb and re-radiate the longer-wavelength infrared heat radiation that the warmed surface emits back toward space; the higher the concentration of CO₂, the more of this outgoing heat radiation is absorbed and trapped within the atmosphere rather than escaping, so global temperature rises as CO₂ concentration increases.

Why are outdoor workers, children, and the elderly considered high-risk groups for poor air quality?

Outdoor workers face prolonged, continuous exposure to ambient pollutant levels rather than brief exposure, increasing their cumulative dose; children under 18 have developing respiratory and immune systems that are more vulnerable to damage, while adults over 65 and people with existing chronic heart or lung disease have reduced physiological reserve to cope with the added stress that pollutants place on the cardiovascular and respiratory systems.

Why is PM_{2.5} generally considered more harmful to health than PM₁₀?

PM_{2.5} particles are small enough (2.5 micrometers or less) to penetrate deep into the lungs and even enter the bloodstream, causing inflammation, cardiovascular strain, and long-term organ damage, whereas the larger PM₁₀ particles are more often trapped by the nose and upper airways before reaching the deep lung tissue; because PM_{2.5} reaches further into the body and is harder for the respiratory system to filter out, it poses a greater health risk at the same mass concentration.



How does a catalytic converter reduce three different types of vehicle pollutants at once?

A catalytic converter uses catalysts to drive three separate reactions simultaneously inside a single unit: it oxidizes carbon monoxide (CO) to carbon dioxide (CO₂), reduces nitrogen oxides (NO_x) back to harmless nitrogen gas (N₂), and oxidizes unburnt hydrocarbons to carbon dioxide and water vapour, converting three classes of harmful exhaust pollutants into far less harmful products before they leave the tailpipe.

Why does effective air pollution control require international cooperation rather than only national laws?

Air pollutants such as CFCs, greenhouse gases, and windblown particulate matter do not stay confined within the borders of the country that released them; they can travel via wind and water currents to affect people, wildlife, and climate far from their source, so a country acting alone cannot fully protect its own air quality, making coordinated international agreements and governance necessary alongside domestic laws and regulations.

Long Questions & Answers

Explain how chlorofluorocarbons (CFCs) cause depletion of the ozone layer, and describe the wider role of the atmosphere's temperature-defined layers in this process.

What are CFCs, and how do they reach the stratosphere where ozone depletion occurs?

CFCs are organic compounds containing chlorine and fluorine that exist as gases or low-boiling liquids at room temperature and were widely used as aerosol propellants and refrigerants; being chemically stable and long-lived in the lower atmosphere, they gradually diffuse upward through the troposphere and stratosphere until UV radiation in the stratosphere is intense enough to break them apart.



What is the first step of the ozone-depletion mechanism, and what species does it produce?

UV radiation breaks a C-Cl bond in the CFC molecule, shown as $\text{CFCI}_3 \xrightarrow{\text{UV}} \text{CFCI}_2 + \text{Cl} \cdot$; this photolysis step releases a highly reactive chlorine free radical ($\text{Cl} \cdot$) into the stratosphere, which is the species directly responsible for attacking ozone molecules in the following steps.

How does the chlorine free radical destroy ozone, and how is it regenerated afterward?

The chlorine radical reacts with ozone, $\text{Cl} \cdot + \text{O}_3 \rightarrow \text{ClO} \cdot + \text{O}_2$, converting one ozone molecule into ordinary oxygen and a chlorine monoxide radical; this $\text{ClO} \cdot$ radical then reacts with a free oxygen atom, $\text{ClO} \cdot + \text{O} \rightarrow \text{Cl} \cdot + \text{O}_2$, which regenerates the original chlorine radical and releases another O_2 molecule, completing a self-sustaining catalytic cycle.

Why can a single CFC molecule destroy up to 100,000 ozone molecules?

Because the chlorine radical is regenerated rather than consumed at the end of the two-step ozone-destroying cycle, it can immediately react with another ozone molecule and repeat the same two steps many thousands of times before it is eventually removed from the stratosphere by other reactions, meaning its destructive effect is not limited to a single reaction event.

How does the stratosphere's own structure make it especially vulnerable to this process?

The stratosphere is defined by rising temperature with altitude because its upper region absorbs high-energy UV radiation to form ozone, while its middle region sees ozone reform exothermically from monatomic and diatomic oxygen; because this entire protective ozone layer depends on a delicate balance between ozone formation and natural breakdown, introducing an efficient catalytic destroyer like the chlorine radical shifts that balance toward net ozone loss, thinning the very layer that shields the earth's surface from harmful UV radiation.



Explain how burning fossil fuels contributes to both acid rain and the greenhouse effect, and describe how air quality is measured and communicated to the public.

What pollutants does burning fossil fuels release that lead to acid rain, and how do they form acids?

Burning fossil fuels releases sulfur oxides (SO_x) and nitrogen oxides (NO_x) into the atmosphere; SO₂ is oxidized to SO₃ which reacts with water vapour to form sulfuric acid (H₂SO₄), while NO is oxidized to NO₂ which reacts with water to form nitric acid (HNO₃) alongside further NO, and both acids can be carried long distances by wind before falling back to earth as acid rain, hail, snow, or fog.

Why does acid rain remain a serious environmental concern even though it looks and feels like ordinary rain?

Acid rain has a pH below 5.6 and is visually indistinguishable from clean rain, giving no obvious warning of its corrosive potential; despite this unremarkable appearance, its acidity causes widespread damage to soils, water bodies, forests, and man-made structures over time, which is precisely what makes it a serious, easily underestimated environmental hazard.

How does burning fossil fuels separately contribute to the greenhouse effect and global warming?

Fossil fuel combustion releases large quantities of carbon dioxide, a primary greenhouse gas that transmits incoming short-wavelength solar radiation but absorbs and re-radiates the longer-wavelength heat radiation emitted by the warmed earth's surface; as atmospheric CO₂ concentration rises from continued fossil fuel use, more of this outgoing heat is trapped rather than lost to space, driving the long-term rise in global average surface temperature known as global warming.

What is the Air Quality Index (AQI), and what do its different bands communicate to the public?

The AQI is a numeric measure of pollutant concentration at a given location, running from 0 to 500 and divided into six colour-coded bands of increasing



health concern: Good (0-50, green), Moderate (51-100, yellow), Unhealthy for Sensitive Groups (101-150, orange), Unhealthy (151-200, red), Very Unhealthy (201-300, purple), and Hazardous (301-500, maroon), letting the public quickly judge whether it is safe to spend time outdoors.

What methods do environmental engineers use to actually measure the pollutant concentrations behind the AQI?

Direct measurement methods include continuous emission monitoring systems (CEMS) that track gases like CO, O₃, SO₂, NO₂, VOCs, and PM at industrial sites, fixed air quality monitoring stations (AQMS) equipped with sensors in urban and industrial areas for real-time data, and satellite-based remote sensing techniques that measure atmospheric pollutants over large regional or global areas; instruments such as the nephelometer measure particulate matter specifically by detecting the light that suspended particles scatter.

Multiple Choice Questions (MCQs)

Which gas causes the yellow-brown colour associated with photochemical smog?

- A. CO
- B. SO₃
- C. NO₂
- D. SO₂

Answer: C. NO₂

Explanation: Nitrogen dioxide (NO₂) absorbs visible light in a way that gives photochemical smog its characteristic yellow-brown haze, distinguishing it from the greyish industrial smog caused mainly by sulfur oxides.

The depletion of ozone in the stratosphere is mainly due to the reaction of O₃ with which class of compounds?

- A. CO₂
- B. SO₂
- C. O₂
- D. CFCs

Answer: D. CFCs

Explanation: Chlorofluorocarbons (CFCs) diffuse into the stratosphere and are



broken down by UV radiation into chlorine free radicals, which catalytically destroy ozone molecules in a repeating chain reaction.

Which particulate matter size is considered most harmful to human health?

- A. PM 10.0
- B. PM 5.0
- C. PM 2.5
- D. PM 1.0

Answer: C. PM 2.5

Explanation: PM2.5 (particles 2.5 micrometers or smaller) can penetrate deep into the lungs and even enter the bloodstream, making it more harmful than the larger, more easily filtered PM10 particles.

Which of the following is a natural factor that can improve air quality?

- A. Wildfire
- B. Urbanization
- C. Rainfall
- D. Industrial emission

Answer: C. Rainfall

Explanation: Rainfall washes particulate matter and soluble pollutants out of the air (a process related to how acid rain forms), naturally improving air quality, whereas wildfires, urbanization, and industrial emissions all add pollutants to the atmosphere.

What is a common human activity that has led to increased levels of carbon monoxide in the atmosphere?

- A. Tree planting
- B. Gasoline-driven vehicles
- C. Using electric appliances
- D. Solar panel installation

Answer: B. Gasoline-driven vehicles

Explanation: Carbon monoxide forms mainly from incomplete combustion of fossil fuels, and gasoline-driven vehicles are a major source of this incomplete combustion, unlike tree planting, electric appliances, or solar panels, which do not directly emit CO.

Chlorofluorocarbons (CFCs) have been primarily used in:



- A. Fertilizers
- B. Refrigerants and aerosol propellants
- C. Pharmaceuticals
- D. Pesticides

Answer: B. Refrigerants and aerosol propellants

Explanation: CFCs exist as gases or low-boiling liquids at room temperature and were widely used as refrigerants and as propellants in aerosol products, which is also how they enter the atmosphere and eventually reach the stratosphere.

What is the primary chemical process that removes carbon dioxide from the atmosphere?

- A. Combustion
- B. Photosynthesis
- C. Respiration
- D. Volcanic activity

Answer: B. Photosynthesis

Explanation: Photosynthesis in plants and other photosynthetic organisms consumes atmospheric CO₂ to produce organic matter and oxygen, making it the main natural process that removes CO₂ from the atmosphere; combustion, respiration, and volcanic activity all add CO₂ instead.

An AQI value between 51 and 100 typically indicates which level of air quality?

- A. Good
- B. Moderate
- C. Unhealthy
- D. Fatal

Answer: B. Moderate

Explanation: On the AQI scale, 0-50 is Good, while 51-100 is classified as Moderate, meaning air quality is acceptable but may pose a slight risk for unusually sensitive individuals.

Acid rain is primarily caused by the release of which of the following gases into the atmosphere?

- A. CO₂ and CH₄
- B. SO₂ and NO_x
- C. CFCs and halons



D. O₃ and CO

Answer: B. SO₂ and NO_x

Explanation: SO₂ and NO_x are oxidized in the atmosphere and react with water vapour to form sulfuric acid and nitric acid respectively, which are the acids responsible for lowering rainwater pH below the 5.6 threshold that defines acid rain.

In the presence of sunlight and nitrogen oxides (NO_x), VOCs primarily contribute to the formation of:

A. Acid rain

B. Ozone depletion

C. Photochemical smog

D. Greenhouse gases

Answer: C. Photochemical smog

Explanation: VOCs and NO_x undergo photochemical reactions in sunlight to produce secondary pollutants like ozone and peroxyacetyl nitrates (PAN), which together with primary pollutants make up photochemical (Los Angeles-type) smog.

Quick Revision Summary

- Atmosphere composition: N₂ 78.00%, O₂ 21.01% (major); Ar 0.93%, CO₂ 0.04% (minor); CH₄, H₂, Ne, He, Kr, Xe (trace)
- Four layers by temperature trend: Troposphere 0-12km (17 to -58°C, weather occurs), Stratosphere 12-50km (-58 to -2°C, ozone layer), Mesosphere 50-80km (-2 to -93°C, coldest), Thermosphere 80-600km (rises to 500-2000°C+)
- Primary pollutants = directly emitted (e.g. CO from exhaust); secondary pollutants = formed from reactions of primary pollutants (e.g. O₃, PAN)
- Major pollutants: CO/CO₂, NO_x, SO_x, hydrocarbons, low-altitude O₃, CFCs, PAHs, POPs, VOCs, PM, heavy metals (Pb, Hg, Cd)
- CFC ozone depletion (catalytic chain): CFCI₃ -UV-> CFCI₂ + Cl. ; Cl. + O₃ -> ClO. + O₂ ; ClO. + O -> Cl. + O₂ (Cl. regenerated, 1 CFC destroys up to 100,000 O₃)
- Smog: Industrial/classical (London, high SO_x) vs Photochemical (Los Angeles, NO_x + VOCs + sunlight -> O₃ + PAN, more dangerous)



- Acid rain ($\text{pH} < 5.6$): $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$, $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$; $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$
- Greenhouse effect: $\text{CO}_2/\text{H}_2\text{O}$ let in short-wave solar radiation but trap outgoing long-wave heat radiation $\rightarrow$ global warming
- AQI bands: 0-50 Good (green), 51-100 Moderate (yellow), 101-150 Unhealthy for Sensitive Groups (orange), 151-200 Unhealthy (red), 201-300 Very Unhealthy (purple), 301-500 Hazardous (maroon)
- Pollution control tech: catalytic converter ($\text{CO} \rightarrow \text{CO}_2$, $\text{NO}_x \rightarrow \text{N}_2$, hydrocarbons $\rightarrow \text{CO}_2 + \text{H}_2\text{O}$), diesel particulate filter, selective catalytic reduction, scrubbers
- Pakistan laws: PEPA 1997, NEQS, Punjab Environmental Protection (Amendment) Act 2012
- Air pollution costs: economic (productivity, crop yield, food prices), social (vulnerable groups, displacement), political (needs international cooperation, crosses borders)

Exam Tips

- Learn the four atmospheric layers as a temperature zig-zag: down (troposphere) - up (stratosphere) - down (mesosphere) - up (thermosphere) -- this pattern alone answers many layer-identification questions
- For CFC ozone depletion, remember the chlorine radical is regenerated, not consumed -- this catalytic aspect is exactly why one CFC molecule can destroy up to 100,000 ozone molecules, a common exam point
- Don't confuse industrial (classical/London) smog with photochemical (Los Angeles) smog -- industrial smog is about SO_x , photochemical smog is about $\text{NO}_x + \text{VOCs} + \text{sunlight}$ producing O_3 and PAN
- For acid rain equations, always show both steps: the oxide first oxidizes further ($\text{SO}_2 \rightarrow \text{SO}_3$, $\text{NO} \rightarrow \text{NO}_2$), then that further-oxidized species reacts with water to form the acid
- Memorize the AQI band boundaries (50, 100, 150, 200, 300) together with their colours -- questions often ask you to match a numeric AQI value to its health-concern level and colour
- When explaining pollution-control technologies, name the specific pollutant each one targets (catalytic converter: CO , NO_x , hydrocarbons; DPF: PM;



scrubbers: PM, SO₂, HCl, NH₃, VOCs) rather than describing them only in general terms



Chapter 15: Basic Separation Techniques

Analytical chemistry is the science of chemical characterization, combining qualitative analysis (identifying which elements or compounds are present) and quantitative analysis (determining their relative amounts); a complete quantitative determination proceeds through sampling, separation of the desired constituent, measurement and calculation, and drawing conclusions. This chapter introduces five basic physical methods used to separate the components of a mixture: filtration, crystallization, simple distillation, fractional distillation, and paper chromatography.

Filtration separates an insoluble solid from a liquid using a filter medium such as filter paper, a Gooch crucible, or a sintered glass crucible; crystallization purifies a solid by dissolving it hot in a suitable solvent and allowing pure crystals to form on cooling; simple distillation separates a dissolved solid from its solvent, while fractional distillation separates two miscible liquids of different boiling points using a fractionating column; and paper chromatography separates a mixture of soluble substances based on their differing distribution between a stationary and a mobile phase, characterized quantitatively by the retardation factor (R_f). Together with melting-point and boiling-point comparisons, these techniques let a chemist both separate a mixture and verify the purity of the resulting product.

Learning Objectives

- Define important terms associated with creating chemical solutions: solvent, solute, solution, residue, and filtrate
- Explain the methods of separation and purification: filtration, crystallization, simple distillation, and fractional distillation
- Identify substances and assess their purity using melting and boiling point information
- Suggest suitable separation and purification techniques given information about substances and their daily-life usage
- Describe how paper chromatography is used to separate mixtures of soluble substances using a suitable solvent



- Describe the use of locating agents when separating mixtures containing colourless substances
- Interpret simple chromatograms to identify unknown substances by comparison with known pure and impure substances
- State and use the formula for the retardation factor (R_f)

Key Concepts

15.1 Filtration

Filtration separates one component of a two-component heterogeneous mixture from a solution, using a solvent in which one component dissolves completely while the other remains insoluble. For example, dissolving a mixture of common salt and sand in distilled water gives a homogeneous solution in which salt (the solute) distributes throughout water (the solvent, the component present in excess), while sand remains undissolved and settles at the bottom; filtration then separates the sand.

Filtration can use filter paper (folded simply, or as fluted filter paper for faster flow through a conical funnel) or a crucible. With filter paper, the liquid that passes through is called the filtrate, and the solid left behind on the paper is called the residue; the filter paper should end up one-fourth to one-half full of precipitate, and porosity is chosen based on particle size. Two types of filtering crucibles are used: the Gooch crucible, porcelain with a perforated bottom covered by paper pulp or filter paper (useful for precipitates that must be ignited at high temperature, and usable with asbestos matting for solutions like concentrated HCl or KMnO_4 that would react with paper), and the sintered glass crucible, which has a porous glass disc sealed into the bottom and needs no preparation.

15.2 Crystallization

Crystallization relies on the principle that a solute is more soluble in a solvent at high temperature than at low temperature, so excess solute is thrown out as crystals on cooling. An ideal solvent for crystallization dissolves a large amount of the substance hot but only a little at room temperature, does not react chemically with the solute, does not dissolve the impurities (or lets them stay in



solution rather than crystallizing with the solute), deposits well-formed crystals on cooling, and is inexpensive, safe, and easily removed; common choices include water, absolute ethanol, chloroform, carbon tetrachloride, and acetic acid, or a combination of miscible solvents if none alone is suitable. If the solvent is flammable, a water bath is used for heating.

The steps of crystallization are: prepare a saturated solution of the substance in a suitable solvent at the experimental temperature; filter the hot saturated solution to remove insoluble impurities (using a hot water funnel if necessary, to avoid premature crystallization choking the filter paper or funnel); cool the hot filtered solution at a moderate rate so medium-sized crystals form; filter the resulting mixture of crystals and mother liquor through a Gooch crucible using a vacuum pump; and finally dry the crystals, either air-dried, in an oven (only if the substance does not melt or decompose at 100 degC), or safely in a vacuum desiccator using a drying agent such as CaCl_2 , silica gel, or phosphorus pentaoxide. Coloured or resinous impurities can be removed by boiling with powdered animal charcoal, which adsorbs the colour, before filtering the hot solution.

15.3 Simple and Fractional Distillation

Simple distillation separates a solvent from a solution -- for example, distilling sea water (a mixture of many soluble inorganic compounds in water) to make it drinkable. Boiling chips are added to prevent bumping, and the apparatus is made airtight; the flask is heated gently, cold water circulates around the condenser, and the vapours that reach their boiling point pass through the condenser and condense back into liquid, collected as the distillate in the receiving flask, while the components left behind in the distillation flask are called the residue.

Fractional distillation separates two miscible liquids of different boiling points, and works successfully only when the boiling points differ by around 25 degC or more; it uses a distillation column packed with glass beads to increase the surface area for condensing vapour. For an ethanol-water mixture, ethanol (boiling point 78 degC) distils over first while the thermometer stays at 78 degC; when the temperature begins rising above 78 degC, the receiving flask is swapped, and heating continues until the temperature reaches 100 degC, at



which point water distils over and is collected as the second distillate, giving both components in pure form. Petroleum, a natural mixture of fuels (petrol, diesel, kerosene, furnace oil) with closely spaced boiling points, is separated into these fractions by fractional distillation in an industrial fractionating column.

15.4 Chromatography: Principles and Types

Chromatography separates a mixture by distributing its components (the solute) between a stationary phase (a solid, or a liquid supported as a thin film on an inert solid) and a mobile phase (a gas or liquid flowing over the stationary phase). When the stationary phase is a solid, the technique is called adsorption chromatography (e.g., thin layer chromatography and column chromatography), in which a substance leaves the mobile phase to become adsorbed on the solid surface; when the stationary phase is a liquid, the technique is called partition chromatography (e.g., paper chromatography and gas-liquid chromatography), in which the substances distribute throughout both phases.

Paper chromatography is a type of partition chromatography in which the entrapped water in cellulose fibres of the paper acts as the (immiscible) stationary phase against an organic mobile phase. It can be run as ascending, descending, or radial/circular chromatography; in the ascending method, the solvent travels upward by capillary action. A sample spot is placed on a pencil line about 2.5 cm from one end of a strip of Whatman's chromatographic paper No.1, alongside spots of known compounds if desired; the paper is suspended with the impregnated end dipping 5-6 mm into solvent inside a covered chromatographic tank, and as the solvent front rises, different components move at different rates, separating the mixture; when the solvent front nears the top, the strip is removed, the front is marked, and the strip is dried.

15.5 Locating Agents and the Retardation Factor (R_f)

The dried, developed pattern on the paper is called a chromatogram. Coloured components can be identified visually, but colourless components must be developed by chemical or physical methods -- viewing under UV light (spots appear coloured) or using a locating agent such as ninhydrin, a chemical that reacts with colourless substances like amino acids to give visible coloured products.



Each component has a characteristic retardation factor, $R_f = (\text{distance travelled by the component from the origin}) / (\text{distance travelled by the solvent from the origin})$. Paper chromatography checks purity: a pure substance gives one spot on the chromatogram, while an impure substance gives more than one; comparing R_f values against known pure samples also allows identification, since two substances with the same R_f under the same conditions are likely identical. Whatman filter paper No.1, made from selected cotton cellulose with medium retention, medium flow rate, and 11 micrometer pore size, is used for routine paper chromatography.

Chromatography is widely used in organic synthesis for separation, isolation, and purification of products, in qualitative and quantitative analysis, for determining the purity of a substance, and for identifying complicated chemicals such as dyes, drugs, and pesticides -- for example, comparing the inks used at different points in a document.

15.6 Checking the Purity of a Product

Liquids are typically purified by distillation (at normal pressure or under vacuum) and their purity checked by comparing the measured boiling point with the literature value. Solids are often purified by crystallization and checked by melting point. As a worked example: aspirin, prepared by reacting salicylic acid with excess acetic anhydride in the presence of a few drops of concentrated H_2SO_4 , is precipitated by adding water, filtered as a crude product, and then crystallized from water.

The crude aspirin may still be mixed with unreacted salicylic acid. Purity is assessed in three ways: (i) melting point -- a pure product melts sharply at exactly 136°C , while an impure product melts over a range of temperatures rather than sharply; (ii) mixed melting point -- mixing the product with a pure sample of aspirin and re-measuring the melting point; if it is still sharp, the product is pure; (iii) paper chromatography -- running the sample alongside pure samples of aspirin and salicylic acid and comparing R_f values.

Important Definitions

What is the difference between a solute and a solvent?



The solute is the substance that dissolves and is present in a smaller amount, while the solvent is the substance in which it dissolves and is present in excess; together they form a homogeneous solution.

What are the filtrate and the residue?

The filtrate is the liquid that passes through the filter medium during filtration, while the residue is the solid material left behind on the filter medium.

What is the basic principle of crystallization?

A solute is more soluble in a suitable solvent at high temperature than at low temperature, so when a hot saturated solution is cooled, the excess solute separates out as pure crystals.

What is a fluted filter paper, and why is it used?

A filter paper folded into a fan-like arrangement with alternate elevations and depressions, which increases the surface area in contact with a conical funnel and considerably speeds up the rate of filtration.

What is the difference between a Gooch crucible and a sintered glass crucible?

A Gooch crucible is porcelain with a perforated bottom that must be covered with paper pulp or filter paper before use and is suited to precipitates that need high-temperature ignition, while a sintered glass crucible has a porous glass disc sealed permanently into the bottom and needs no preparation before use.

What is the essential condition for fractional distillation of two liquids to succeed?

The boiling points of the two liquids being separated must differ by around 25 degC or more; if they are closer than this, a fractionating column cannot cleanly separate them into pure fractions.

What are the stationary phase and mobile phase in paper chromatography?

The stationary phase is the water entrapped within the cellulose fibres of the paper, while the mobile phase is the organic solvent that moves over the paper by capillary action, carrying the sample's components at different rates.

What is a locating agent?



A chemical, such as ninhydrin, that reacts with an otherwise colourless separated substance (like an amino acid) to produce a visible coloured product, allowing its spot on a chromatogram to be identified.

What is the retardation factor (Rf)?

The ratio of the distance travelled by a component from the origin to the distance travelled by the solvent from the origin in a chromatogram; it is a characteristic value for a given substance under given conditions.

How does the number of spots on a paper chromatogram indicate purity?

A pure substance produces exactly one spot on the chromatogram, while an impure substance, being a mixture of two or more components, produces more than one spot.

Key Facts and Relations

Topic	Key Fact / Relation
Retardation factor	$R_f = (\text{distance travelled by component from origin}) / (\text{distance travelled by solvent from origin})$
Fractional distillation feasibility condition	Boiling points of the two liquids should differ by about 25 degC or more
Ethanol-water fractional distillation plateaus	Ethanol distils at 78 degC; water distils at 100 degC
Aspirin pure melting point	Sharp melting point at exactly 136 degC indicates a pure product
Crystallization drying agents (vacuum desiccator)	CaCl ₂ , silica gel, or phosphorus pentoxide (P ₂ O ₅)
Crystallization solvent examples	Water, absolute ethanol, chloroform, carbon tetrachloride, acetic acid
Whatman filter paper No.1 (chromatography)	Medium retention, medium flow rate, pore size 11 micrometers

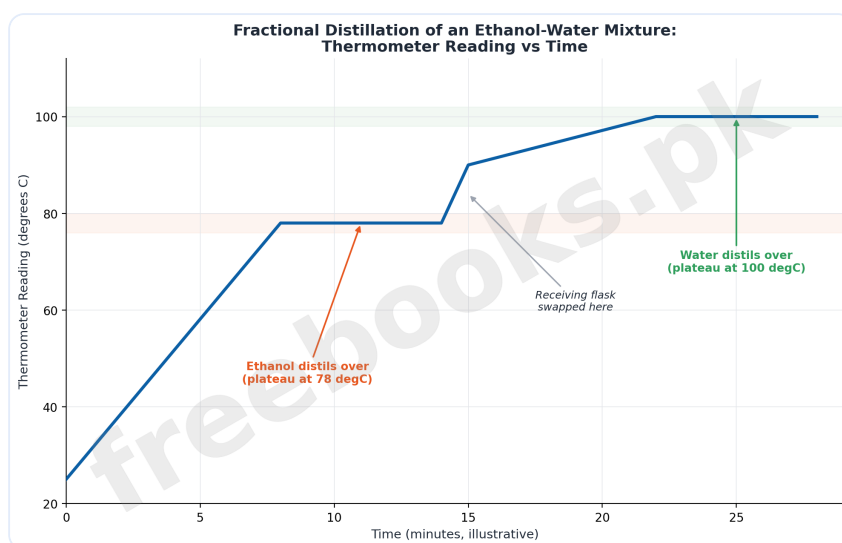


Topic	Key Fact / Relation
Filter paper fill guideline	Filter paper should be one-fourth to one-half full of precipitate at the end of filtration
Paper chromatography spotting distance	Sample spotted about 2.5 cm from one end, on a pencil (not ink) line
Solvent immersion depth (ascending chromatography)	Paper dips 5-6 mm into the solvent in the chromatographic tank

Diagrams

Fractional Distillation of an Ethanol-Water Mixture: Thermometer

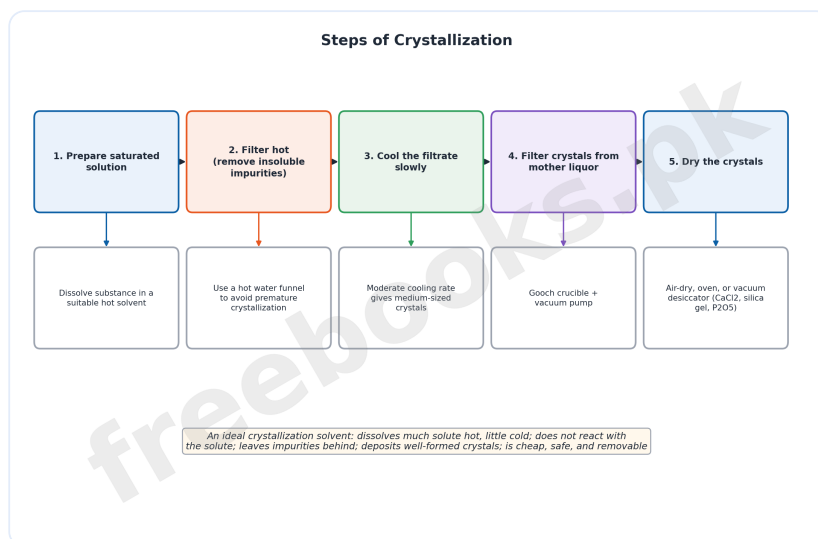
Reading vs Time: A temperature-time plot showing the characteristic plateau at 78 degC while ethanol distils over, the point at which the receiving flask is swapped, and the second plateau at 100 degC while water distils over



Fractional Distillation of an Ethanol-Water Mixture: Thermometer Reading vs Time

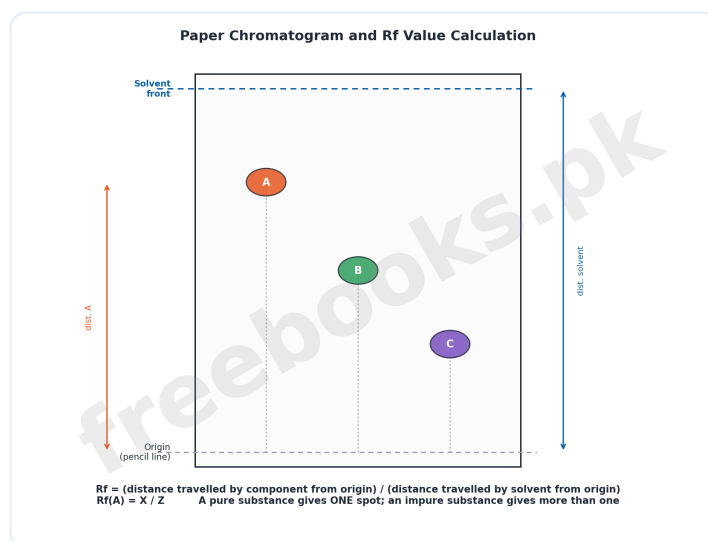
Steps of Crystallization: A five-step flow diagram showing the crystallization process from preparing a saturated solution through hot filtration, controlled cooling, filtering the crystals from the mother liquor, and drying





Steps of Crystallization

Paper Chromatogram and Rf Value Calculation: A labelled chromatogram showing the origin, solvent front, and three separated spots, illustrating how the distance travelled by a component and by the solvent are measured and used to calculate the Rf value



Paper Chromatogram and Rf Value Calculation

Short Questions & Answers

Why must the hot saturated solution be filtered before it is allowed to cool during crystallization?

If insoluble impurities are left in the solution while it cools, they can act as extra surfaces for crystal nucleation or become trapped within the growing crystals, contaminating the final product; filtering the solution while it is still hot removes



these impurities first, and a hot water funnel is used for this step specifically to prevent the dissolved solute from crystallizing prematurely and choking the filter paper or funnel.

Why does the thermometer reading stay constant at 78 degC while ethanol is distilling over in a fractional distillation of ethanol and water?

As long as liquid ethanol is present and boiling, the vapour above it remains at ethanol's boiling point because the energy supplied by heating goes into vaporizing more ethanol rather than raising the temperature further; only once essentially all of the ethanol has distilled over does the remaining liquid start behaving more like pure water, allowing the thermometer reading to rise toward 100 degC.

Why is a Gooch crucible sometimes covered with an asbestos mat instead of paper pulp?

Ordinary filter paper or paper pulp can chemically react with strongly oxidizing or corrosive solutions such as concentrated HCl or KMnO_4 , damaging the filter medium and contaminating the filtrate; covering the perforated crucible bottom with an asbestos mat instead provides a chemically inert filtering surface that can safely be used with such reactive solutions.

Why does paper chromatography rely on the paper's water content rather than the paper itself as the stationary phase?

In partition chromatography, separation depends on how a component distributes between two immiscible liquid phases; the actual stationary phase in paper chromatography is the water trapped within the cellulose fibres of the paper (which is immiscible with the usually organic mobile phase), not the solid cellulose fibres themselves, so it is this entrapped water layer that governs how strongly each component is retained as the mobile phase moves past it.

Why would water generally be an unsuitable solvent to use as the mobile phase in paper chromatography?

Since the stationary phase in paper chromatography is itself water held within the cellulose fibres, using water as the mobile phase as well would eliminate the two-phase partition system the technique depends on, because the mobile and stationary phases would then be miscible (in fact identical) rather than



immiscible, preventing the differential distribution of components that produces separation.

Why is a fractionating column packed with glass beads rather than left as a plain, empty tube?

Packing the column with glass beads greatly increases the internal surface area available for vapour to repeatedly condense and re-evaporate as it rises through the column; each cycle of condensation and re-evaporation enriches the vapour in the more volatile component, so a packed column achieves a much sharper separation between two liquids with similar boiling points than an empty tube would.

Why does a sharp, well-defined melting point indicate that a solid product is pure, while a broad melting range suggests it is impure?

A pure crystalline solid has a uniform, well-ordered lattice in which every particle experiences essentially identical intermolecular forces, so the entire sample melts within a very narrow temperature range; the presence of an impurity disrupts this uniform lattice structure at various points throughout the solid, weakening it unevenly and causing melting to begin at a lower temperature and continue gradually over a broader range rather than sharply at one exact temperature.

Why is a mixed melting point test more conclusive than measuring the melting point of the sample alone?

If an unknown or impure-looking sample is mixed with a genuine pure sample of the suspected substance and the melting point remains just as sharp as before, this confirms the two samples are the same substance, because mixing two different substances would normally lower and broaden the melting point through mutual lattice disruption; a sharp mixed melting point rules out this depression effect and provides stronger evidence of both identity and purity than a single melting-point measurement alone.

Why can two substances with different chemical identities sometimes need more than just their R_f value to be confidently distinguished?

R_f values, while characteristic of a substance under a fixed solvent system and set of conditions, can coincidentally match between two chemically different substances or can shift slightly with small variations in solvent composition, temperature, or paper batch, so matching R_f values alone provides strong but



not absolute evidence of identity; running known reference spots alongside the unknown on the very same chromatogram under identical conditions strengthens the comparison considerably.

Why is filtration through a Gooch or sintered glass crucible generally faster than filtration through an ordinary filter paper and funnel?

Suction filtration through a crucible uses a vacuum pump to actively draw the liquid through the porous crucible bottom, creating a pressure difference that pulls the filtrate through far more quickly than gravity alone can achieve with an ordinary filter paper and funnel, where the liquid can only pass through as fast as gravity drains it.

Long Questions & Answers

Describe the process of crystallization in detail, including the choice of solvent and the individual steps involved, and explain how crystallization differs from simple filtration as a purification technique.

What features should an ideal solvent for crystallization have?

An ideal crystallization solvent should dissolve a large amount of the substance at its boiling point but only a small amount at room temperature (so cooling throws out plenty of pure solute as crystals), should not react chemically with the solute, should either not dissolve the impurities or should not let them crystallize alongside the solute, should deposit well-formed crystals of the pure compound on cooling, and should be inexpensive, safe to use, and easily removable from the final product.

What is the first step of crystallization, and why must the solution be saturated?

The first step is to prepare a saturated solution of the crude substance in a suitable solvent at the temperature of the experiment; the solution must be saturated because crystallization depends on there being more dissolved solute than the solvent can hold once it cools, so starting from a saturated hot solution



ensures that cooling will force a substantial, purifiable amount of solute out of solution as crystals rather than leaving it all dissolved.

Why is the hot solution filtered before it is allowed to cool, and what precaution prevents this step from failing?

The hot saturated solution is filtered to remove any insoluble impurities before crystallization begins, since leaving them in the solution during cooling could trap them within the forming crystals or use them as extra nucleation sites; because crystals can sometimes begin forming during this filtration step itself and choke the filter paper or funnel, a hot water funnel is used to keep the solution hot enough to filter cleanly.

What happens during the cooling and final filtration steps, and why does cooling rate matter?

The hot filtered solution is cooled at a moderate rate, which allows medium-sized, well-formed crystals to grow (cooling too quickly tends to produce many small, impure crystals, while cooling too slowly is impractical); once crystallization is complete, the mixture of crystals and mother liquor is filtered through a Gooch crucible using a vacuum pump to separate the crystals from the remaining liquid.

How does crystallization as a purification technique differ fundamentally from simple filtration?

Filtration separates an insoluble solid from a liquid based purely on particle size and solubility, physically trapping undissolved particles on a filter medium while dissolved substances pass through in the filtrate; crystallization, by contrast, purifies a solid that is itself soluble by exploiting the difference in its solubility at high versus low temperature, converting a dissolved impure solute into a solid of much higher purity through controlled cooling, rather than simply separating dissolved and undissolved material as filtration does.



Explain how paper chromatography separates a mixture of soluble substances, how the retardation factor (R_f) is defined and used, and how these principles allow the purity of a product like aspirin to be checked.

What physical principle allows paper chromatography to separate the components of a mixture?

Paper chromatography is a form of partition chromatography in which the water entrapped in the cellulose fibres of the paper acts as an immiscible stationary phase against an organic mobile phase that moves up the paper by capillary action; because different components of the sample have different relative affinities for the stationary versus the mobile phase, they are carried up the paper at different rates, separating them into distinct spots.

How is a paper chromatogram practically set up and run using the ascending method?

A sample is spotted on a pencil line about 2.5 cm from one end of a strip of Whatman No.1 chromatographic paper, often alongside spots of known reference compounds; once the spots have dried, the paper is suspended in a covered chromatographic tank with the spotted end dipping 5-6 mm into a solvent mixture, and as the solvent rises up the paper by capillary action, the different components move upward at their own characteristic rates, separating the original mixture into distinct spots.

How is the R_f value calculated, and what does it represent?

The R_f value is calculated as the distance travelled by a given component from the origin divided by the distance travelled by the solvent front from the same origin; because this ratio is characteristic of a particular substance under a particular set of solvent and paper conditions, it provides a reproducible numerical fingerprint that can be used to identify or compare substances between different chromatography runs.



How does the number of spots and their R_f values help determine whether a product is pure?

A pure substance, since it consists of only one chemical species, produces exactly one spot on the finished chromatogram, whereas an impure product, containing more than one substance, produces two or more spots at different positions corresponding to their different R_f values; comparing the R_f value of an unknown spot to that of a known pure reference run on the same chromatogram under the same conditions also allows the identity of an unknown substance to be confirmed.

How would paper chromatography specifically be used to check whether a sample of crude aspirin is pure?

The crude aspirin sample would be run on the same chromatogram alongside pure reference samples of both aspirin and its likely contaminant, unreacted salicylic acid, using a suitable solvent system; if the aspirin sample produces only a single spot that matches the R_f value of the pure aspirin reference spot exactly, with no separate spot appearing at the R_f value of salicylic acid, this indicates the sample is free of unreacted starting material and is chromatographically pure.

Multiple Choice Questions (MCQs)

After crystals are formed, they are typically separated from the mother liquor by:

- A. Evaporation
- B. Decantation or filtration
- C. Sublimation
- D. Distillation

Answer: B. Decantation or filtration

Explanation: Once crystallization is complete, the mixture of solid crystals and remaining liquid (mother liquor) is separated by filtration (commonly through a Gooch crucible with a vacuum pump) or by carefully decanting off the liquid, not by evaporation, sublimation, or distillation.



The comparative rates at which solutes move in paper chromatography depend on:

- A. Size of filter paper
- B. R_f values of solutes
- C. Temperature of the room only
- D. Size of the chromatographic jar

Answer: B. R_f values of solutes

Explanation: Each solute moves at a rate characteristic of its own retardation factor (R_f), which reflects how it partitions between the stationary and mobile phases; this is what differentiates the movement rates of different components in the mixture.

Which method can be used to separate two solid compounds with different solubilities in a solvent?

- A. Distillation
- B. Isolation
- C. Crystallization
- D. Filtration

Answer: C. Crystallization

Explanation: Crystallization exploits the difference in solubility of two solid compounds in a given solvent, particularly the difference between their solubility at high versus low temperature, to selectively crystallize out one compound in pure form while the other remains dissolved.

Which technique would be used to check whether the inks used at different points of a hand-written document are the same?

- A. Distillation
- B. Chromatography
- C. Solvent extraction
- D. Crystallization

Answer: B. Chromatography

Explanation: Chromatography (typically paper or thin layer chromatography) can separate the dye components of different inks and compare their patterns and R_f values, revealing whether the inks used at different points of a document match or differ.



In chromatography, the components of a mixture are separated based on:

- A. Their molecular masses only
- B. The interaction of the components with stationary and mobile phases
- C. The type of solvent used only
- D. The filter paper used only

Answer: B. The interaction of the components with stationary and mobile phases

Explanation: Separation in chromatography arises from the differing degree to which each component interacts with (partitions between or adsorbs onto) the stationary phase versus the mobile phase, causing components to move at different rates.

The porous material used to separate the solid from the liquid during filtration is called the:

- A. Filtrate
- B. Residue
- C. Filter medium
- D. Solvent

Answer: C. Filter medium

Explanation: The filter medium (such as filter paper, a Gooch crucible, or a sintered glass crucible) is the porous material through which the liquid passes; the liquid that passes through is the filtrate and the solid left behind is the residue.

The key difference between simple distillation and fractional distillation is the presence of a:

- A. Condenser with a larger surface area
- B. More powerful heat source
- C. Fractionating column
- D. Vacuum pump

Answer: C. Fractionating column

Explanation: Fractional distillation adds a fractionating column, typically packed with glass beads to increase surface area for repeated condensation and re-evaporation, allowing it to separate two miscible liquids of similar boiling points; simple distillation has no such column.



The essential requirement for separating two liquids by simple distillation (as opposed to needing fractional distillation) is that their boiling points should differ by at least:

- A. 5 degC
- B. 10 degC
- C. 25 degC
- D. 50 degC

Answer: C. 25 degC

Explanation: A boiling point difference of around 25 degC or more is generally needed for the components to be separated cleanly; below this, a plain distillation setup cannot resolve the two liquids and a fractionating column (fractional distillation) becomes necessary.

What is the mobile phase in paper chromatography usually composed of?

- A. Water entrapped in the paper fibres
- B. An organic liquid solvent
- C. A solid adsorbent
- D. Compressed inert gas

Answer: B. An organic liquid solvent

Explanation: The mobile phase in paper chromatography is usually an organic liquid solvent that moves up (or across) the paper by capillary action, while the stationary phase is the water held within the cellulose fibres of the paper itself.

A crude sample of aspirin is found to melt gradually over a range of temperatures rather than sharply at 136 degC. What does this most likely indicate?

- A. The sample is completely pure
- B. The sample is impure, likely still containing some starting material
- C. The sample has an unusually high molecular weight
- D. The measurement was taken at the wrong pressure

Answer: B. The sample is impure, likely still containing some starting material

Explanation: A pure crystalline substance melts sharply at one exact temperature; a broad, gradual melting range instead indicates the presence of impurities (such as unreacted salicylic acid) disrupting the crystal lattice, so the sample is impure.



Quick Revision Summary

- Filtration separates insoluble solid from solution; filtrate = liquid that passes through, residue = solid left behind on the filter medium
- Filter media: filter paper (plain or fluted for speed), Gooch crucible (porcelain, needs paper pulp/asbestos, for high-temp/reactive solutions), sintered glass crucible (porous glass disc, no prep needed)
- Crystallization: dissolve hot in a suitable solvent -> filter hot (remove insoluble impurities) -> cool slowly (medium crystals) -> filter crystals from mother liquor (Gooch crucible + vacuum) -> dry (air/oven/vacuum desiccator with CaCl_2 , silica gel, or P_2O_5)
- Ideal crystallization solvent: dissolves much hot, little cold; doesn't react with solute; doesn't dissolve/co-crystallize impurities; gives well-formed crystals; cheap, safe, removable
- Simple distillation separates dissolved solid from solvent (e.g. sea water -> drinking water); distillate collected, residue left in flask
- Fractional distillation separates two miscible liquids (boiling points differ by $\sim 25^\circ\text{C}$) using a glass-bead-packed fractionating column; e.g. ethanol (78°C) distils before water (100°C)
- Chromatography: distributes solute between stationary phase (solid = adsorption chromatography; liquid = partition chromatography) and mobile phase (gas or liquid)
- Paper chromatography = partition chromatography; stationary phase = water in cellulose fibres; mobile phase = organic solvent; ascending type most common (capillary action)
- Colourless spots located via UV lamp or a locating agent (e.g. ninhydrin, reacts with amino acids to give colour)
- R_f = distance travelled by component / distance travelled by solvent (both measured from the origin); pure substance = 1 spot, impure = more than 1 spot
- Purity checks: liquids by comparing boiling point to literature value; solids by sharp melting point (e.g. pure aspirin melts sharply at 136°C) or mixed melting point; either can also use matching R_f values



Exam Tips

- Keep the four key terms straight: solute (dissolves, minor amount), solvent (dissolves it, major amount), filtrate (liquid through the filter), residue (solid left on the filter) -- exam questions often test these definitions directly
- For Gooch vs sintered glass crucible questions, remember Gooch needs paper pulp/asbestos prep and suits high-temperature ignition, while sintered glass needs zero preparation and is simply reusable
- For crystallization, always list the steps in the correct order: dissolve hot -> filter hot -> cool slowly -> filter crystals -> dry -- questions often ask 'what step comes next' or 'why filter while hot'
- Remember the numeric threshold for fractional vs simple distillation: liquids need a boiling point difference of about 25 degC or more to be separated by fractional distillation with a packed column
- For chromatography, don't confuse the two classifications: adsorption chromatography = solid stationary phase; partition chromatography = liquid stationary phase (paper chromatography is partition, not adsorption)
- Always write the R_f formula as component distance over solvent distance, both measured from the same origin -- and remember R_f has no units, since it is a ratio of two distances



Chapter 16: Lab Safety and Practical Skills

A chemistry laboratory is a chemist's workshop, a place where students are trained to observe the physical and chemical characteristics of substances by following definite procedures. Before starting laboratory work, students must follow general safety instructions, understand the three main categories of laboratory hazards (physical, chemical, and biological), know the correct system for chemical waste disposal, and be prepared to give first aid for common laboratory accidents such as cuts, eye injuries, burns, poisoning, and fire.

This chapter also develops core practical skills: performing an acid-base titration using a burette, pipette, and a suitable indicator to locate the end point and calculate an unknown molarity, and carrying out qualitative salt analysis -- identifying acid radicals (anions) such as carbonate, chloride, bromide, iodide, nitrate, and sulfate, and basic radicals (cations) such as aluminium, ammonium, calcium, chromium, copper, iron(II), iron(III), and zinc, using characteristic reagent tests, precipitate colours, and confirmatory reactions.

Learning Objectives

- Identify chemical hazards in the lab in the context of the experiment being conducted
- Test that equipment is working properly, without risk of injury, before starting an experiment
- Keep the workspace uncrowded and maintain a safe distance from other investigators handling apparatus
- Identify the bodily harm that can occur from physical, chemical, biological, and safety hazards
- Recognize when to ask the lab instructor for help with unfamiliar apparatus
- Identify the proper waste disposal system for laboratory chemicals
- Set up apparatus following written or diagrammatic instructions, and make careful, repeatable measurements and observations
- Describe acid-base titration, including the use of a burette, volumetric pipette, and suitable indicator, and how to identify the end point



- Select reagents to distinguish between given anions and cations, and describe the standard confirmatory tests for each

Key Concepts

16.1 General Laboratory Instructions

Students must conduct themselves responsibly at all times and should never work alone in the lab; experiments should be performed in the presence of the lab instructor and other staff. Lab coats and safety goggles must always be worn, with long hair and scarves tied back. Potential hazards of any equipment or experiment must be determined before starting work, and appropriate precautions observed.

The lab should never be crowded, and students must keep a safe distance from each other's work areas. Food is not permitted in the lab, and no compound or gas should ever be tasted or smelled directly. Any accident or glassware breakage must be reported immediately to the person in charge. Students who cannot handle an instrument properly must seek help from the instructor rather than risk injury. Chemicals must never be poured down drains or into the sewer system, and all warning signs displayed in the lab must be followed.

16.2 Types of Laboratory Hazards

Laboratory hazards fall into three broad categories. Physical hazards are most commonly slips and falls on wet floors; workers must take precautions against slipping, tripping, and falling, and should wear cut-resistant gloves when handling broken glassware to prevent cuts and abrasions, with broken glass disposed of in a special container to prevent injury.

Chemical hazards require using chemicals strictly according to standard procedures, with attention to the specific hazards and precautions indicated by hazard pictograms for each substance. Biological hazards are most commonly allergens and microbes (viruses and bacteria), which can be transferred to humans from animals, plants, water, and air.



16.3 Waste Disposal and First Aid

Chemical waste cannot be disposed of in ordinary bins or the sewer system; it must follow Environmental Protection Agency (EPA) rules: store wastes in proper containers, label each container with the type of waste, the date, and its place of origin, transfer containers to an allocated treatment site, and treat the waste chemically (neutralization, precipitation, ion exchange, oxidation, or reduction) before disposal.

Every laboratory must have a first aid box. Key treatments include: for minor cuts, apply methylated spirit or tincture iodine as a disinfectant, while serious cuts need firm pressure for about 10 minutes and a doctor's attention; for acid in the eye, wash with water then 1% sodium bicarbonate solution, and for alkali in the eye, wash with water then 1% boric acid solution; for acid burns, wash freely with ice-cold water, then saturated sodium bicarbonate solution, then water again; for alkali burns, wash with water, then 1% acetic acid solution, then water, dry, and apply burnol; for bromine burns, wash fully with 2% ammonia solution and apply glycerin. Swallowed acid calls for plenty of water, lime water, or milk of magnesia; swallowed caustic alkali calls for plenty of water followed by lemon or orange juice; swallowed heavy metal salts call for milk or egg white. For fires: if clothes catch fire, do not run, wrap with a blanket or dry cloth and lie down; for a flask of flammable liquid on fire, smother it with a damp cloth to cut off oxygen; for spirit or oil fires, throw a sand and sodium bicarbonate mixture (never water, which spreads the fire); for electrical fires, switch off the power immediately and use sand, never water.

16.4 Acid-Base Titration

Volumetric analysis finds the concentration of a solution by titration: a solution of unknown concentration is combined slowly with a known volume of a standard solution until a colour change (produced by an indicator) shows the reaction is complete, a moment called the end point. Either the acid or the base is placed in a burette, with the other in a conical (titration) flask.

Procedure: rinse the pipette with distilled water then with the NaOH solution, and pipette 10 cm³ of NaOH into a rinsed conical flask; add 1-2 drops of phenolphthalein (solution turns pink); rinse and fill the burette with HCl using a



funnel, remove any air bubble from the tip, and note the initial burette reading using an anti-parallax card; place the flask on white paper under the burette, and add acid drop-wise while swirling the flask continuously, until the colour changes to a persistent light pink -- this is the end point; note the final burette reading, and repeat the titration to obtain at least three concordant readings agreeing within 0.1 cm³. The volume of acid used is the difference between final and initial burette readings.

The reaction is $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$. The unknown molarity is found from $M_1V_1/n_1 = M_2V_2/n_2$, where M_1 , V_1 , n_1 are the molarity, volume, and number of moles (in the balanced equation) of the acid, and M_2 , V_2 , n_2 are the corresponding values for the base.

16.5 Identification of Anions (Acid Radicals)

Carbonate (CO_3^{2-}): adding dilute HCl to a solid carbonate sample produces brisk effervescence; the gas evolved turns lime water milky, confirming carbonate ($\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$; $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$).

Chloride, bromide, and iodide: dissolve the solid sample in water, acidify with dilute HNO_3 (to prevent carbonate ions from also precipitating), then add aqueous AgNO_3 . Chloride gives a thick white precipitate that dissolves in aqueous ammonia ($\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$, white ppt); bromide gives a thick cream-yellow precipitate ($\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$); iodide gives a bright yellow precipitate ($\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}$).

Nitrate (NO_3^-): dissolve the sample, add sodium hydroxide solution, then powdered aluminium metal; a characteristic smell of ammonia is felt and the gas turns red litmus blue, since aluminium reduces nitrate to ammonium, which reacts with NaOH to evolve ammonia gas ($3\text{NO}_3^- + 8\text{Al} + 5\text{OH}^- + 18\text{H}_2\text{O} \rightarrow 3\text{NH}_3 + 8[\text{Al(OH)}_4]^-$).

Sulfate (SO_4^{2-}): dissolve the sample, acidify with dilute HNO_3 (to destroy any carbonate impurity), then add barium nitrate solution; a heavy white precipitate of BaSO_4 forms ($\text{SO}_4^{2-} + \text{Ba}^{2+} \rightarrow \text{BaSO}_4$).



16.6 Identification of Cations (Basic Radicals)

Each cation is tested by dissolving a solid sample in distilled water, dividing it into two portions, and treating one with NaOH solution and the other with aqueous ammonia, comparing the precipitate colour and its behaviour in excess reagent. Al^{3+} gives a white gelatinous precipitate with NaOH (insoluble in excess) and a white precipitate with aqueous ammonia ($\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3$). NH_4^+ evolves ammonia gas with a distinct smell on gentle heating with NaOH, turning moist red litmus blue ($\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$).

Ca^{2+} gives a white precipitate with NaOH that does not dissolve in excess, and only slight turbidity (or no precipitate) with aqueous ammonia ($\text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{Ca}(\text{OH})_2$). Cr^{3+} gives a green precipitate with NaOH that dissolves in excess NaOH, but a green precipitate insoluble in excess aqueous ammonia ($\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr}(\text{OH})_3$, green ppt). Cu^{2+} gives a light-blue precipitate with NaOH ($\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2$) but a deep blue solution with aqueous ammonia as a soluble copper-ammonia complex forms.

Fe^{2+} gives a green precipitate with NaOH that turns orange-brown on standing as it oxidizes, and a white gelatinous precipitate of $\text{Fe}(\text{OH})_2$ with aqueous ammonia that quickly oxidizes to red-brown $\text{Fe}(\text{OH})_3$ ($\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$, green ppt). Fe^{3+} gives an orange-brown precipitate with both NaOH and aqueous ammonia ($\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$, orange-brown ppt). Zn^{2+} gives a white precipitate with NaOH that is soluble in excess NaOH, and a white precipitate with aqueous ammonia that is also soluble in excess ammonia ($\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2$, white ppt).

Important Definitions

What is an indicator in a titration?

A substance that shows the completion of a reaction by a visible change in its colour, used to signal when the acid and base in a titration have reacted in stoichiometric proportions.

What is the end point of a titration?

The moment during a titration at which the indicator changes colour, signalling that the reaction between the two solutions is essentially complete.



What is a concordant reading in titration?

Two or more titration readings that agree closely with one another, typically within 0.1 cm³, used to confirm the accuracy and reliability of the titration result.

What are physical hazards in a laboratory?

Hazards such as slips, trips, and falls (often caused by wet floors) and injuries from handling broken glassware, which can be reduced by taking precautions and wearing cut-resistant gloves.

What are biological hazards in a laboratory?

Hazards such as allergens and microbes, including viruses and bacteria, which can be transferred to humans from animals, plants, water, or air present in or around the laboratory.

Why must chemical waste never be poured down the sewer or drains?

Because most chemical wastes are hazardous to the environment and human health if released untreated, so EPA rules require they be stored in labelled containers, transferred to an allocated site, and chemically treated (e.g., neutralization, precipitation, ion exchange, oxidation, or reduction) before disposal.

Why is dilute HNO₃ added before testing a solution with AgNO₃ for halide ions?

Dilute nitric acid is added to prevent carbonate ions from also precipitating alongside the halide ions when silver nitrate is added, ensuring that any precipitate observed is due specifically to the halide ion being tested for.

What colour precipitates confirm chloride, bromide, and iodide ions with silver nitrate?

Chloride gives a thick white precipitate (AgCl) that dissolves in aqueous ammonia; bromide gives a thick cream-yellow precipitate (AgBr); iodide gives a bright yellow precipitate (AgI).

How is nitrate ion (NO₃⁻) identified in salt analysis?

By dissolving the sample, adding sodium hydroxide solution, then powdered aluminium metal; a characteristic smell of ammonia gas is produced (which turns red litmus blue), since aluminium reduces nitrate ions to ammonium ions that react with the NaOH to release ammonia gas.



How is sulfate ion (SO₄²⁻) identified in salt analysis?

By dissolving the sample, acidifying with dilute nitric acid, and adding barium nitrate solution; a heavy white precipitate of barium sulfate (BaSO₄) confirms the presence of sulfate ions.

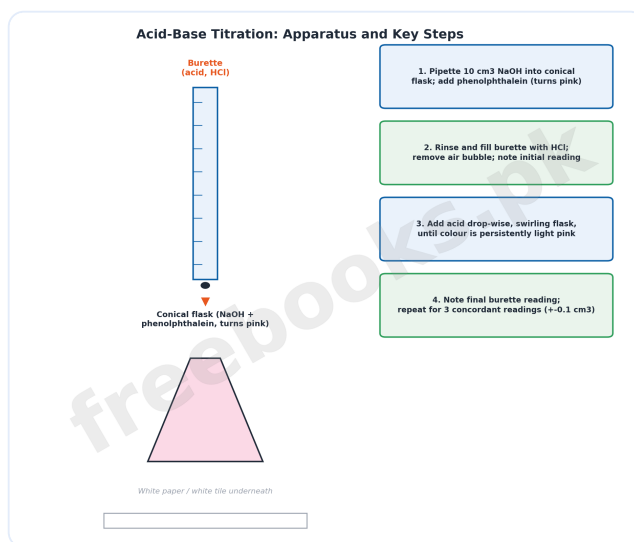
Key Facts and Relations

Topic	Key Fact / Relation
Titration end-point equation (acid-base)	$\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
Molarity relation for titration calculation	$M_1V_1/n_1 = M_2V_2/n_2$ (M=molarity, V=volume, n=moles in balanced equation)
Concordant reading tolerance	Titration readings should agree within about 0.1 cm ³
Carbonate test	$\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$ (gas turns lime water milky)
Halide + AgNO ₃ precipitate colours	AgCl = white, AgBr = cream-yellow, AgI = bright yellow
Nitrate test (with Al and NaOH)	$3\text{NO}_3^- + 8\text{Al} + 5\text{OH}^- + 18\text{H}_2\text{O} \rightarrow 3\text{NH}_3 + 8[\text{Al(OH)}_4]^-$
Sulfate test	$\text{SO}_4^{2-} + \text{Ba}^{2+} \rightarrow \text{BaSO}_4$ (heavy white precipitate)
Al ³⁺ /Ca ²⁺ /Cr ³⁺ /Fe ²⁺ /Fe ³⁺ /Zn ²⁺ hydroxide precipitation	$\text{Mn}^{2+} + n\text{OH}^- \rightarrow \text{M(OH)}_n$ (precipitate colour depends on the metal)
Distinguishing feature: Cr ³⁺ vs Al ³⁺ with excess NaOH	Both dissolve in excess NaOH, but Cr(OH) ₃ is green while Al(OH) ₃ is white
Distinguishing feature: Fe ²⁺ vs Fe ³⁺	Fe ²⁺ gives a green ppt that turns orange-brown on standing; Fe ³⁺ gives an orange-brown ppt immediately



Diagrams

Acid-Base Titration: Apparatus and Key Steps: A labelled schematic of the burette and conical flask setup, together with the four key procedural steps from pipetting the base to recording concordant burette readings



Acid-Base Titration: Apparatus and Key Steps

Summary of Anion (Acid Radical) Identification Tests: A colour-coded reference table listing the reagents added and the resulting observation for carbonate, chloride, bromide, iodide, nitrate, and sulfate ions

Summary of Anion (Acid Radical) Identification Tests		
Anion	Reagent Added	Observation (Inference)
Carbonate (CO ₃ ²⁻)	+ dilute HCl	Effervescence; gas turns lime water milky
Chloride (Cl ⁻)	+ dil. HNO ₃ , then AgNO ₃	Thick white ppt; dissolves in aq. NH ₃
Bromide (Br ⁻)	+ dil. HNO ₃ , then AgNO ₃	Thick cream-yellow ppt
Iodide (I ⁻)	+ dil. HNO ₃ , then AgNO ₃	Bright yellow ppt
Nitrate (NO ₃ ⁻)	+ NaOH, then Al powder	Smell of NH ₃ ; turns red litmus blue
Sulfate (SO ₄ ²⁻)	+ dil. HNO ₃ , then Ba(NO ₃) ₂	Heavy white ppt of BaSO ₄

Summary of Anion (Acid Radical) Identification Tests

Cation (Basic Radical) Identification: Precipitate with NaOH vs Aqueous NH₃: A comparison table showing the precipitate colour and behaviour in excess



reagent for eight common cations when treated separately with NaOH solution and aqueous ammonia

Cation (Basic Radical) Identification: Precipitate with NaOH vs Aqueous NH ₃		
Cation	+ NaOH solution	+ Aqueous NH ₃
Al ³⁺	White gelatinous ppt, insoluble in excess NaOH	White ppt (insoluble in excess)
Ca ²⁺	White ppt, insoluble in excess NaOH	Slight turbidity or no ppt
Cr ³⁺	Green ppt, dissolves in excess NaOH	Green ppt, insoluble in excess
Cu ²⁺	Light blue ppt	Deep blue solution (complex forms)
Fe ²⁺	Green ppt → turns orange-brown on standing	White gelatinous ppt → oxidizes red-brown
Fe ³⁺	Orange-brown ppt	Orange-brown ppt
Zn ²⁺	White ppt, soluble in excess NaOH	White ppt, soluble in excess

Cation (Basic Radical) Identification: Precipitate with NaOH vs Aqueous NH₃

Short Questions & Answers

Why should students never work alone in a chemistry lab?

Working alone removes the safety net of having a lab instructor or other staff present who can immediately assist if an accident, chemical spill, or equipment malfunction occurs; the presence of others allows for a quick response to injuries, immediate first aid, and someone to fetch help, all of which can be critical in the first moments after a laboratory accident.

Why is dilute nitric acid added before testing for sulfate ions with barium nitrate?

Barium ions would also form an insoluble precipitate with any carbonate ions present as an impurity in the sample, which could be mistaken for the barium sulfate precipitate that confirms sulfate; adding dilute nitric acid first destroys any carbonate impurity by converting it to carbon dioxide and water, ensuring that a white precipitate observed after adding barium nitrate is due specifically to sulfate.

Why must the conical flask be swirled continuously while acid is added during a titration?

Swirling ensures the acid being added drop by drop mixes thoroughly and rapidly throughout the whole volume of solution in the flask, rather than reacting only in



the local region where it lands; without thorough mixing, the indicator could show a local, temporary colour change near the point of addition that does not reflect the true, overall state of the reaction, causing the end point to be misjudged.

Why is an anti-parallax card or white paper used when reading the burette scale?

Reading a scale from an angle rather than exactly at eye level introduces a systematic error called parallax, which can make the meniscus appear at a different graduation than its true position; an anti-parallax card, usually marked with a dark line, helps the reader align their eye level exactly with the meniscus, minimizing this reading error and improving the precision of the recorded volume.

Why does copper(II) hydroxide dissolve in excess aqueous ammonia but not in excess NaOH?

Aqueous ammonia can act as a ligand and coordinate directly to the copper(II) ion, forming a soluble deep-blue tetraamminecopper(II) complex ion that redissolves the initially formed light-blue hydroxide precipitate as more ammonia is added; hydroxide ions from NaOH, in contrast, do not form an analogous soluble complex with copper(II) under these conditions, so the light-blue $\text{Cu}(\text{OH})_2$ precipitate simply remains once formed.

Why does the green precipitate formed when NaOH is added to an Fe^{2+} solution turn orange-brown on standing?

The precipitate formed is iron(II) hydroxide, $\text{Fe}(\text{OH})_2$, in which iron is in the +2 oxidation state; on standing in air, atmospheric oxygen gradually oxidizes the iron(II) hydroxide to iron(III) hydroxide, $\text{Fe}(\text{OH})_3$, which has the characteristic orange-brown colour, so the colour change over time is a direct visible sign of aerial oxidation occurring at the precipitate's surface.

Why are both aluminium hydroxide and zinc hydroxide soluble in excess NaOH, while calcium hydroxide is not?

Aluminium and zinc hydroxides are amphoteric, meaning they can react with excess hydroxide ions to form soluble complex ions (such as $[\text{Al}(\text{OH})_4]^-$ and $[\text{Zn}(\text{OH})_4]^{2-}$), allowing the initially formed precipitate to redissolve as more NaOH is added; calcium hydroxide is not amphoteric and does not form an analogous



soluble hydroxide complex, so it remains as an insoluble precipitate even in excess NaOH.

Why is a fire caused by burning oil or spirit smothered with sand and sodium bicarbonate rather than extinguished with water?

Oil, spirit, and other flammable liquids are less dense than water and do not mix with it, so pouring water onto such a fire causes the burning liquid to float and spread across the water's surface, actually enlarging the fire rather than extinguishing it; sand and sodium bicarbonate instead smother the fire by physically covering it and cutting off its oxygen supply, which is the safe and effective way to extinguish this type of fire.

Why is it important to rinse the pipette with the solution to be measured (not just distilled water) before use?

Any residual distilled water left inside the pipette from washing would dilute the solution subsequently drawn into it, introducing an error into the measured volume and concentration of that solution; rinsing the pipette first with the actual solution to be measured displaces any remaining water and ensures the solution finally drawn up is at its true, undiluted concentration.

Why does a solid carbonate sample effervesce with dilute HCl while producing a gas that turns lime water milky?

Carbonate ions react with the hydrogen ions from the acid to release carbon dioxide gas, which is seen as brisk effervescence (bubbling) as the gas escapes the solution; when this carbon dioxide gas is passed into lime water (a solution of calcium hydroxide), it reacts to form insoluble calcium carbonate, which appears as a milky, cloudy precipitate suspended in the liquid, confirming the presence of carbonate ions in the original sample.



Long Questions & Answers

Describe the procedure for carrying out an acid-base titration between a standard HCl solution and an NaOH solution of unknown concentration, and explain how the results are used to calculate the unknown molarity.

How is the conical flask prepared before the titration begins?

The pipette is first rinsed with distilled water and then with the NaOH solution to remove any residual water that could dilute it; the conical flask is rinsed with distilled water only (since it will not affect the amount of NaOH once pipetted in); 10 cm³ of NaOH solution is then pipetted into the flask, and one to two drops of phenolphthalein indicator are added, turning the solution pink.

How is the burette prepared and its initial reading recorded?

The burette is rinsed first with distilled water and then with the HCl solution, filled using a funnel (which is then removed), and any air bubble trapped in the nozzle is cleared by briefly allowing acid to flow into a waste beaker; the burette is fixed upright on a clamp stand, and the initial reading is noted carefully using an anti-parallax card or white paper to avoid parallax error.

How is the actual titration carried out to locate the end point?

With the conical flask placed on white paper beneath the burette (to see the colour change clearly) and checked for leaks, acid is first added quickly in a rough titration to get an approximate end point, then in a careful, drop-wise titration while continuously swirling the flask to ensure thorough mixing, until the pink colour turns to a persistent light pink -- this is the end point of the reaction.

Why is the titration repeated, and what result is taken forward for calculation?

The titration is repeated to obtain at least three concordant readings that agree with one another within about 0.1 cm³, since a single reading could be affected by an error in judging the end point; taking the volume from concordant



readings, rather than a single titration, gives a more reliable and accurate value for the volume of acid actually needed to neutralize the base.

How is the unknown molarity of the NaOH solution calculated from the titration data?

Using the molarity relation $M_1V_1/n_1 = M_2V_2/n_2$, where M_1 and V_1 are the known molarity and volume of the acid used and n_1 is the number of moles of acid in the balanced equation, while M_2 , V_2 , and n_2 are the corresponding values for the base, the equation is rearranged to $M_2 = (M_1V_1/n_1) \times (n_2/V_2)$; substituting the concordant titration volume, the known acid molarity, and the mole ratio from the balanced equation $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ (where $n_1 = n_2 = 1$) gives the unknown molarity of the NaOH solution.

Explain how qualitative salt analysis is used to identify unknown anions and cations, describing the specific tests and observations used to distinguish chloride, bromide, and iodide ions, and to distinguish iron(II) from iron(III) ions.

What is the general strategy behind qualitative salt analysis?

Qualitative salt analysis identifies the ions present in an unknown solid sample by dissolving it and treating separate portions with specific reagents, then observing characteristic changes such as precipitate formation, precipitate colour, gas evolution, or colour change, each of which is uniquely associated with a particular anion or cation and therefore acts as confirmatory evidence for its presence.

What common test distinguishes chloride, bromide, and iodide ions from one another?

All three halide ions are tested by acidifying the sample solution with dilute nitric acid (to prevent interference from carbonate ions) and then adding aqueous silver nitrate; the resulting precipitate's colour differs distinctly between the three ions, allowing them to be told apart using the same basic test.



What specific precipitate colours are observed for chloride, bromide, and iodide with silver nitrate?

Chloride ions produce a thick white precipitate of silver chloride, which notably dissolves when aqueous ammonia is added; bromide ions produce a thick cream-yellow precipitate of silver bromide; and iodide ions produce a bright yellow precipitate of silver iodide, giving three visually distinguishable outcomes from the same basic silver nitrate test.

What test distinguishes Fe^{2+} (iron II) from Fe^{3+} (iron III) ions?

Both ions are tested by adding NaOH solution or aqueous ammonia to a sample solution; Fe^{2+} initially gives a green precipitate of iron(II) hydroxide that gradually turns orange-brown on standing in air as it is oxidized to iron(III) hydroxide, while Fe^{3+} gives an orange-brown precipitate of iron(III) hydroxide immediately, with no initial green stage, allowing the two iron oxidation states to be distinguished by both the initial precipitate colour and how that colour changes (or does not change) over time.

Why is it useful to test a sample with both NaOH and aqueous ammonia rather than just one reagent?

Different cations can sometimes give a similarly coloured precipitate with just one reagent, but their behaviour in excess of that reagent, or their behaviour with the second reagent, often reveals a clear difference; for example, Al^{3+} and Zn^{2+} both give a white precipitate with NaOH, but $\text{Al}(\text{OH})_3$ stays insoluble in excess aqueous ammonia while $\text{Zn}(\text{OH})_2$ dissolves in excess ammonia, so testing with both reagents and observing behaviour in excess provides more complete and unambiguous confirmatory evidence than either reagent alone.

Multiple Choice Questions (MCQs)

While reading a burette, why is it advisable to read the lower meniscus for colourless liquids and the upper meniscus for coloured liquids?

- A. Because it is more convenient
- B. Because colourless liquids have more surface tension than coloured liquids
- C. Because the lower meniscus does not exist for coloured liquids



D. Because the upper surface of a coloured liquid is easier to see clearly against the lower meniscus, which is often obscured by the liquid's own colour

Answer: D. Because the upper surface of a coloured liquid is easier to see clearly against the lower meniscus, which is often obscured by the liquid's own colour

Explanation: For coloured liquids, the curve of the lower meniscus can be difficult to see clearly through the coloured solution itself, so the upper meniscus (the top edge of the liquid surface, easier to see against the tube) is read instead; for colourless liquids, the lower meniscus is clearly visible and is the standard reference point.

Why is phenolphthalein indicator particularly appropriate for titrations between a strong acid and a strong base?

- A. Because it is itself weakly acidic
- B. Because the pH range over which phenolphthalein changes colour matches the pH at the equivalence point of a strong acid-strong base titration
- C. Because the solution at the end of titration is acidic
- D. Because the solution at the end of titration is basic

Answer: B. Because the pH range over which phenolphthalein changes colour matches the pH at the equivalence point of a strong acid-strong base titration

Explanation: A strong acid-strong base titration has an equivalence point at pH 7, and the steep pH jump around this point spans a wide pH range that includes phenolphthalein's colour-change range (about pH 8.2-10), making it a suitable and commonly used indicator for this type of titration.

Which cation gives a white gelatinous precipitate upon addition of aqueous ammonia?

- A. Cr^{3+}
- B. Cr^{2+}
- C. Zn^{2+}
- D. Al^{3+}

Answer: D. Al^{3+}

Explanation: Al^{3+} produces a white gelatinous precipitate of aluminium hydroxide, $\text{Al}(\text{OH})_3$, when aqueous ammonia is added, which remains insoluble in excess ammonia, distinguishing it from other cations.



Addition of aqueous ammonia (NH_4OH) to a solution of a cation gives a green precipitate that turns brown on standing. Which basic radical is indicated?

- A. Cu^{2+}
- B. Cr^{3+}
- C. Fe^{2+}
- D. Fe^{3+}

Answer: C. Fe^{2+}

Explanation: Fe^{2+} gives a green precipitate of iron(II) hydroxide with aqueous ammonia (or NaOH), which slowly oxidizes in air to orange-brown iron(III) hydroxide, a characteristic colour change used to identify Fe^{2+} .

The evolution of a colourless, odourless gas that turns lime water milky during salt analysis suggests the presence of:

- A. Chloride ion (Cl^-)
- B. Sulfate ion (SO_4^{2-})
- C. Carbonate ion (CO_3^{2-})
- D. Nitrate ion (NO_3^-)

Answer: C. Carbonate ion (CO_3^{2-})

Explanation: Carbonate ions react with acid to release carbon dioxide gas, which is colourless and odourless and turns lime water milky by forming insoluble calcium carbonate, a classic confirmatory test for carbonate.

A thick cream-yellow precipitate forms when aqueous silver nitrate is added to an acidified salt solution. Which anion does this indicate?

- A. Chloride (Cl^-)
- B. Bromide (Br^-)
- C. Iodide (I^-)
- D. Sulfate (SO_4^{2-})

Answer: B. Bromide (Br^-)

Explanation: Bromide ions form a thick cream-yellow precipitate of silver bromide (AgBr) with silver nitrate, distinguishing it from the white precipitate of chloride and the bright yellow precipitate of iodide.

What is the correct first-aid treatment for an acid burn on the skin?

- A. Apply burnol directly without washing
- B. Wash freely with ice-cold water, then a saturated solution of sodium



bicarbonate, then water again

C. Wash with 2% ammonia solution and apply glycerin

D. Apply mustard oil directly to the burn

Answer: B. Wash freely with ice-cold water, then a saturated solution of sodium bicarbonate, then water again

Explanation: An acid burn should first be washed freely with ice-cold water to remove and dilute the acid, then washed with a saturated sodium bicarbonate solution to neutralize any remaining acid, and finally rinsed again with water before further treatment.

Why should water never be used to extinguish a fire caused by burning oil or spirit?

A. Water reacts explosively with oil

B. Water is denser than oil and sinks below it, making no difference to the fire

C. Water does not mix with the flammable liquid and can cause it to float and spread, enlarging the fire

D. Water evaporates too quickly to have any cooling effect

Answer: C. Water does not mix with the flammable liquid and can cause it to float and spread, enlarging the fire

Explanation: Because oil and spirit are immiscible with and less dense than water, pouring water onto such a fire causes the burning liquid to spread across the water's surface, enlarging rather than extinguishing the fire; sand or a damp cloth is used instead to smother it.

In an acid-base titration, what does a 'concordant reading' refer to?

A. Any single accurate titration reading

B. Two or more titration readings that agree closely with one another, typically within 0.1 cm³

C. The very first rough titration performed

D. The reading taken only at the exact theoretical equivalence point

Answer: B. Two or more titration readings that agree closely with one another, typically within 0.1 cm³

Explanation: Concordant readings are two or more titre volumes from repeated titrations that agree closely with each other (usually within 0.1 cm³), providing confidence that the recorded volume is accurate and not affected by a one-off error in judging the end point.



Which basic radical gives a light-blue precipitate with NaOH solution but forms a deep blue solution when aqueous ammonia is added in excess?

- A. Fe^{2+}
- B. Cr^{3+}
- C. Cu^{2+}
- D. Zn^{2+}

Answer: C. Cu^{2+}

Explanation: Cu^{2+} gives a light-blue precipitate of copper(II) hydroxide with NaOH, but with excess aqueous ammonia, the precipitate dissolves to form a deep blue soluble copper-ammonia complex, a characteristic and easily recognized behaviour for identifying Cu^{2+} .

Quick Revision Summary

- Lab safety: never work alone, wear lab coat/goggles, tie back hair, no food/tasting/smelling chemicals, report accidents immediately, never pour chemicals down the drain
- Three hazard categories: physical (slips, falls, broken glass), chemical (follow standard procedures, hazard pictograms), biological (allergens, viruses, bacteria)
- Chemical waste disposal (EPA rules): store in labelled containers (waste type, date, origin) → transfer to allocated site → treat chemically (neutralization, precipitation, ion exchange, oxidation/reduction)
- First aid basics: acid in eye → water then 1% NaHCO_3 ; alkali in eye → water then 1% boric acid; acid burn → ice water then NaHCO_3 then water; oil/spirit fire → sand + NaHCO_3 , never water
- Titration: indicator shows completion by colour change; end point = moment indicator changes colour; concordant readings agree within 0.1 cm^3
- Titration formula: $M_1V_1/n_1 = M_2V_2/n_2$ (subscript 1 = acid, subscript 2 = base, n = moles in balanced equation)
- Anion tests: CO_3^{2-} (HCl → effervescence, gas turns lime water milky); Cl⁻/Br⁻/I⁻ (AgNO_3 → white/cream-yellow/bright yellow ppt); NO_3^- (NaOH + Al → NH_3 smell, turns litmus blue); SO_4^{2-} ($\text{Ba}(\text{NO}_3)_2$ → heavy white ppt)



- Cation tests (NaOH vs aq. NH_3): Al^{3+} white ppt (insoluble both); Ca^{2+} white ppt with NaOH, slight/no ppt with NH_3 ; Cr^{3+} green ppt (dissolves in excess NaOH, insoluble in excess NH_3); Cu^{2+} light-blue ppt with NaOH, deep blue solution with NH_3 ; Fe^{2+} green ppt $\rightarrow$ orange-brown; Fe^{3+} orange-brown ppt immediately; Zn^{2+} white ppt (soluble in excess of both)
- Amphoteric hydroxides that dissolve in excess NaOH: $\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, $\text{Cr}(\text{OH})_3$ (but $\text{Cr}(\text{OH})_3$ does NOT dissolve in excess aqueous ammonia)

Exam Tips

- Memorize the three hazard categories (physical, chemical, biological) with one clear example of each -- exam questions often ask for two examples per category
- For eye and burn first aid, always remember the pattern: wash with water first, THEN apply the specific neutralizing/soothing agent, THEN wash with water again -- don't skip the initial plain-water wash
- For titration questions, always state that the pipette is rinsed with the solution it will measure (not just distilled water) -- this is a commonly tested precaution
- For halide precipitate colours, remember the trend: chloride = white, bromide = cream-yellow, iodide = bright yellow -- getting the shade order right (not just 'coloured vs white') is often what's actually tested
- For cation identification, focus on what happens in EXCESS reagent, not just the initial precipitate colour -- many cations look similar at first (e.g. white ppt) but behave very differently once excess NaOH or ammonia is added
- Remember Fe^{2+} gives a green precipitate that slowly turns orange-brown (oxidation over time), while Fe^{3+} gives orange-brown immediately with no green stage -- this timing difference is the key distinguishing feature between the two

